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# EFFECT OF STORAGE CONDITIONS ON WEATHERING OF COMMERCIAL GLASS CONTAINERS*

By J. S. Owens and E. C. Emanuel

Abstract

Important factors in the weathering of commercial flint glass containers were determined by the storage of empty bottles, capped and uncapped, of ten different compositions for periods up to thirteen months at (1) 100°F., 80% relative humidity, (2) 120°F., 15% relative humidity, and (3) normal room conditions. The effect of storage was determined by visual inspection, tests of the alkali extraction by water at elevated temperatures, and photomicrographs of the weathered surfaces. The results obtained indicate that the most important factor in the weathering conditions used is the humidity. Although the weathering produced depends on several factors, the important weathering effect of high humidity may be significantly controlled by the chemical composition of the glass. Storage for the periods used at low relative humidity or at normal room conditions was relatively ineffective for weathering any of the bottles tested. Photomicrographs of representative weathered internal and external bottle surfaces are shown. A microscopic examination of these surfaces revealed the presence of calcite.

## I. Introduction

During the storage of empty bottles, the glass surface may be coated with a more or less uniform film or crystalline deposits as a result of weathering. Even though no coating is visible, a film may be present which may be washed from the surface.

Ford[1] classified the weathering obtained on bottles of different compositions into three types; he determined the nature of the weathering products; and he drew certain conclusions relating to the effects of the storage condition, the glass composition, and the nature of the glass surfaces on the type of weathering produced.

Turner and his colleagues[2] have conducted more recent weathering experiments with storage at normal atmospheric conditions in several locations about the laboratories at Sheffield, England, as well as at room temperature with relative humidities of zero and 76% in special chambers. The 5-hour boiling-water test of the Society of Glass Technology[3] was used to determine the chemical durability of the bottles after storage.

The present investigation was undertaken to determine the effects of chemical composition, humidity, temperature, and capping on the weathering and on the subsequent chemical durability of empty bottles stored under controlled conditions.

## II. Ware Tested

Commercial 8-oz. bottles of two compositions and 4-oz. bottles of eight different compositions were used; the 4-oz. bottles were placed in storage at the conclusion of the initial tests of the 8-oz. size.

The 8-oz. bottles, manufactured about two months before the start of the investigation, were received uncapped and in the usual corrugated paper cartons. The 4-oz. commercial bottles, obtained directly before

* Presented in part at the Forty-Third Annual Meeting, The American Ceramic Society, Baltimore, Md., April 1, 1941 (Glass Division). Received February 4, 1942.

[1] K. L. Ford, "Weathering of Glass Containers," *Jour. Amer. Ceram. Soc.*, 5 [12] 837–53 (1922).

[2] (*a*) Violet Dimbleby, H. S. Y. Gill, and W. E. S. Turner, "Effect of Storage on the Chemical Durability of Glass Containers," *Jour. Soc. Glass Tech.*, 19 [75] 231–43T (1935); *Ceram. Abs.*, 15 [2] 58 (1936).

(*b*) Violet Dimbleby and W. E. S. Turner, "Effects of Humidity on the Weathering of Bottle Glasses," *Jour. Soc. Glass Tech.*, 23 [98] 242–52T (1939); *Ceram. Abs.*, 19 [2] 42 (1940).

[3] (*a*) "Standard Test and Specification for the Chemical Durability of 4-Oz. Flat Medicine Bottles," *Jour. Soc. Glass Tech.*, 15, 52–58P (1931).

(*b*) W. E. S. Turner and Associates, "Basis of a Standard Test for the Chemical Durability of Glass Bottles," *Jour. Soc. Glass Tech.*, 19, 171–88T (1935); *Ceram. Abs.*, 16 [7] 200 (1937).

testing, were received capped (except bottle J) in the usual paper cartons. None of the bottles exhibited any visible weathering when received. The capacity, internal surface area, and chemical composition of each type are given in Table I.

No adjustments were made in the following experimental results to compensate for the differences in internal area of the two 8-oz. bottles and among the eight 4-oz. bottles.

## III. Storage Conditions

### (1) Eight-Ounce Bottles

Four cartons of each type of ware were used. One half of the bottles in each carton were uncapped, and the remainder were capped with molded screw caps containing Vinylite-faced, cork composition liners. The bottles were capped under normal atmospheric conditions at room temperature when they were received.

One closed carton of each type of ware was stored with the bottles upright for twelve months at each of the conditions (*a*), (*b*), (*c*), and (*d*) shown in Table II. Representative samples were then removed for photographic and chemical tests, and the cartons which contained the remaining bottles were stored for nine additional months at condition (*e*).

The temperature and humidity conditions in the controlled storage locations (*a*) and (*c*) were maintained rather accurately at the values given in Table II. The conditions in the storerooms, (*d*), (*e*), and (*f*), were subject to the normal fluctuations of an average room. The humidity values for the storerooms are based on monthly noon averages for the warmer months and on monthly averages of frequent measurements made during the colder months when the rooms were heated.

### (2) Four-Ounce Bottles

Three cartons of each type of ware were used. One half of the bottles in each carton were uncapped. The remainder (except bottles G and J) were capped with metal screw caps containing Vinylite-faced pulp liners; bottles G and J were stoppered with Vinylite-covered corks. The closures were applied under normal atmospheric conditions at room temperature when the bottles were received. One closed carton of each type of ware was stored with the bottles upright for thirteen months at each of the conditions (*a*), (*c*), and (*f*) in Table II.

## IV. Experimental Results on Eight-Ounce Bottles

### (1) Visual Examination

The bottles were inspected and photographed at the end of twelve months of storage. Most of the uncapped A bottles stored at controlled conditions (see (*a*) Table II) and approximately one half of the B bottles stored at controlled and storeroom conditions (see (*b*) Table II) contained some condensed moisture; the remaining bottles were apparently dry.

The molded caps on the bottles stored at condition (*a*) and at (*b*) increased in weight and in dimensions as a result of the absorption of moisture and were therefore somewhat loose; the caps on the bottles stored at (*c*) and at (*d*) were tight.

The amount of weathering of each bottle was visually estimated, and this estimate was transformed into a weathering grade by means of the water-solubility and

TABLE I

CAPACITY, INTERNAL AREA, AND CHEMICAL COMPOSITION

| Bottle designation | Capacity (oz.) | Internal area ($cm.^2$) | Chemical composition (%) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | $SiO_2$ | $Na_2O + K_2O$ | CaO | MgO | $Al_2O_3$ | BaO | $B_2O_3$ | $Fe_2O_3$ |
| A | 8 | 266 | 73.06 | 16.01 | 4.87 | 3.42 | 1.08 | 0.75 | 0.75 | 0.055 |
| B | 8 | 250 | 69.68 | 14.40 | 6.36 | 4.32 | 3.69 | 0.57 | 0.92 | 0.060 |
| C | 4 | 155 | 71.73 | 15.86 | 9.16 | 0.52 | 1.58 | 0.26 | 0.83 | 0.060 |
| D | 4 | 162 | 71.63 | 17.22 | 5.02 | 3.49 | 1.68 | 0.05 | 0.86 | 0.055 |
| E | 4 | 153 | 72.61 | 16.36 | 5.35 | 3.47 | 1.60 | 0.08 | 0.46 | 0.070 |
| F | 4 | 149 | 73.31 | 15.95 | 5.58 | 3.35 | 1.05 | 0.24 | 0.46 | 0.065 |
| G | 4 | 159 | 72.08 | 14.47 | 6.76 | 4.38 | 1.43 | 0.51 | 0.33 | 0.060 |
| H | 4 | 159 | 73.26 | 15.29 | 5.43 | 4.07 | 1.14 | 0.42 | 0.33 | 0.060 |
| I | 4 | 151 | 71.98 | 15.30 | 5.92 | 4.00 | 2.04 | 0.42 | 0.28 | 0.060 |
| J | 4 | 162 | 71.38 | 14.49 | 6.06 | 4.00 | 2.54 | 0.50 | 0.96 | 0.075 |

TABLE II

STORAGE CONDITIONS

| Room condition | Temp. (°F.) | | | Humidity | | | | Storage |
|---|---|---|---|---|---|---|---|---|
| | | | | | Grains of $H_2O$/lb. dry air | | | |
| | Avg. | Max. | Min. | Relative (%) | Avg. | Max. | Min. | |
| (*a*) Controlled | 100 | | | 80 | 236 | | | Continuously |
| (*b*) Controlled | 100 | | | 80 | 236 | | | Intermittently* |
| (*b*) Storeroom | 68 | 99 | 30 | Variable | 53 | 85 | 26 | Intermittently* |
| (*c*) Controlled | 120 | | | 15 | 75 | | | Continuously |
| (*d*) Storeroom | 68 | 99 | 30 | Variable | 53 | 85 | 26 | " |
| (*e*) " | 68 | 100 | 25 | " | 59 | 86 | 40 | " |
| (*f*) " | 72 | 100 | 36 | " | 61 | 86 | 27 | " |

* Cyclic storage conditions are 2 days at 100°F., 80% relative humidity, and 2 days at storeroom temperature and humidity.

chemical durability tests. The weathering grade gives an approximate, relative measure of the amount of water-soluble, alkaline weathering product on the internal surface of the bottle. None of the bottles stored at 120°F., and 15% relative humidity, or at normal room conditions exhibited visible weathering. The results for the bottles stored at conditions (*a*) and (*b*) are given in Table III.

TABLE III

VISUAL DETERMINATION OF WEATHERING

| Bottle | Weathering grade Avg. | Max. | Min. | Appearance of avg. grade bottle |
|---|---|---|---|---|
| Storage at 100°F., 80% relative humidity continuously | | | | |
| A* | 46 | 135† | 22 | Translucent coating |
| A | 30 | 74 | 16 | Light translucent coating |
| B* | 1.1 | 2 | 0.6 | Isolated cloudy areas |
| B | 1.7 | 2 | 1.1 | Slight general cloudiness |
| Storage at 100°F., 80% relative humidity intermittently | | | | |
| A* | 40 | 135† | 22 | Translucent coating |
| A | 40 | 54 | 30 | Translucent coating |
| B* | 1.1 | 2 | 0.6 | Isolated cloudy areas |
| B | 0.9 | 2 | 0.6 | Isolated cloudy areas |

* Capped bottles.
† Heavy, uniform opaque coating.

The lower portion of the bottle generally exhibited the greater amount of visible weathering, whereas the upper part of the shoulder and the neck showed little weathering. Figure 1 shows representative bottles of different weathering grades, all stored at 100°F., 80% relative humidity. Grades 0.6, 1.1, and 2.0 are illustrated by bottles B; grades 22, 40, 74, and 135, by bottles A. Table III and Fig. 1 show the greatly superior resistance of bottles B to severe weathering conditions as well as the varied degree of weathering of the different bottles of the same type at the same storage condition. The average appearance of bottles A and B, capped and uncapped, after storage at 100°F., 80% relative humidity, is shown by the bottles of grades 40 and 1.1, respectively. The most advanced visible weathering suffered by an A bottle and by a B bottle is shown by the bottles of grades 135 and 2.0, respectively.

The inspection of the remaining bottles, after nine additional months of storage at normal room conditions, revealed no essential differences between the appearance of the bottles at the end of the first twelve months and of the nine additional months.

## (2) Alkali Extraction Tests

Alkali extraction tests were made at the end of twelve months of storage on capped and uncapped bottles of average weathering grade of each type from each storage location.

The amount of water-soluble weathering product, determined as alkali by titration, on the internal and external surfaces was obtained by immersion of the bottle to within 2.5 cm. of the top in doubly distilled, boiled water, contained in a Pyrex-brand beaker at 50°C. for 6.5 hr. The solutions in contact with the internal and external surfaces of the bottle were boiled and titrated while hot with 0.02 *N* $H_2SO_4$ to a methyl red end point. The results, after correction for the blank, are expressed in Table IV in milligrams of NaOH per liter of solution.

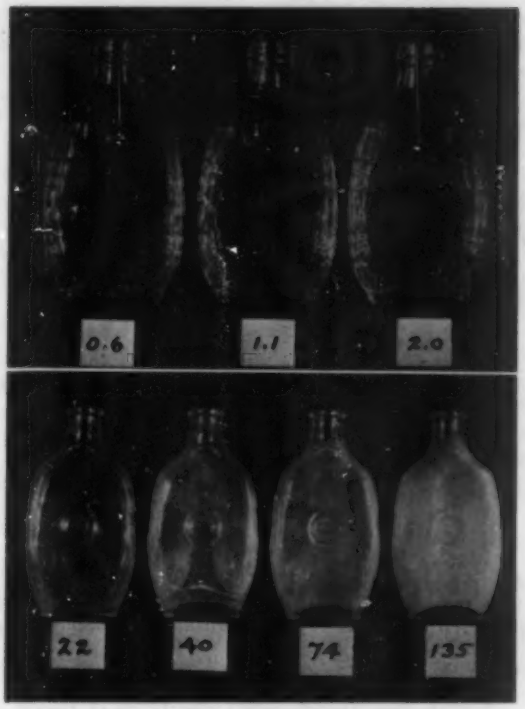


FIG. 1.—Representative bottles of different weathering grades.

The amount of alkali extracted from the internal surface of the bottle by a common autoclave method, referred to hereafter as chemical durability, was determined as follows. Each bottle was rinsed with 40 ml. of doubly distilled, boiled water. Immediately after introducing the water, the bottle was covered with tinfoil and shaken three times so that the water covered the entire internal surface. The bottle was then emptied, filled to rated capacity with similar water, and capped loosely with tinfoil. Pyrex-brand Erlenmeyer flasks of 250-ml. capacity, similarly rinsed, filled, and capped, were placed in the autoclave with the bottles to serve as blank controls. The temperature of the autoclave was raised to 100°C. in approximately 15 minutes and to 120°C. in 15 additional minutes, maintained at this temperature for 60 minutes, and lowered to 100°C. in 30 minutes. After removal from the autoclave, a 100-ml. aliquot of the solution from each bottle was titrated while hot with 0.02 *N* $H_2SO_4$ to a methyl red end point. The results, after correction for the blank, are expressed in Table IV as milligrams of NaOH per liter of solution.

Similar alkali-extraction tests were made at the end of the additional nine months of storage at normal room conditions. The amount of alkali extracted at 120°C. for one hour, from the internal surfaces of bottles not rinsed before the test was determined (Table IV).

TABLE IV

ALKALI EXTRACTION BY WATER

| Bottle (1) | Storage condition: Temperature (°F.) (2) | Storage condition: Relative humidity (%) (3) | Alkali extracted (mgm. of NaOH/liter): Storage, 12 mo.: 50°C., 6.5 hr.: Internal surface (4) | Storage, 12 mo.: 50°C., 6.5 hr.: External surface† (5) | Storage, 12 mo.: 120°C., 1 hr.: Rinsed (6) | Storage, 21 mo.‡: 50°C., 6.5 hr.: Internal surface (7) | Storage, 21 mo.‡: 50°C., 6.5 hr.: External surface† (8) | Storage, 21 mo.‡: 120° C., 1 hr.: Rinsed (9) | Storage, 21 mo.‡: 120° C., 1 hr.: Not rinsed (10) |
|---|---|---|---|---|---|---|---|---|---|
| A* | 100 | 80 | 182 | 89 | 235 | 184 | 106 | 289 | 269 |
| A | continuously | | 167 | 80 | 109 | 146 | 76 | 99 | 182 |
| B* | Same as above | | 3.0 | 3.7 | 6.6 | 3.4 | 2.0 | 4.2 | 8.7 |
| B | | | 12 | 4.6 | 11 | 11 | 2.0 | 12 | 17 |
| A* | 100 | 80 | 264 | 105 | 225 | 227 | 81 | 233 | 259 |
| A | intermittently | | 123 | 100 | 102 | 134 | 82 | 103 | 132 |
| B* | Same as above | | 4.7 | 3.6 | 5.9 | 4.2 | 0.8 | 5.6 | 8.7 |
| B | | | 8.0 | 1.3 | 8.5 | 5.8 | 1.2 | 8.9 | 13 |
| A* | 120 | 15 | 1.0 | 1.3 | 2.9 | | | 5.4 | 2.8 |
| A | | | 1.1 | 1.7 | 3.1 | | | 4.0 | 3.5 |
| B* | Same as above | | 0.9 | 2.2 | 3.8 | | | 2.8 | 3.3 |
| B | | | 0.8 | 2.3 | 4.3 | | | 3.5 | 4.3 |
| A* | Avg. 68; variable | | 1.8 | 2.1 | 11 | | | 12 | 14 |
| A | room conditions | | 1.6 | 3.0 | 15 | | | 13 | 12 |
| B* | Same as above | | 1.4 | 2.1 | 4.2 | | | 3.0 | 4.0 |
| B | | | 1.2 | 1.9 | 3.6 | | | 3.3 | 4.5 |

* Capped bottles
† Corrected to same total volume of solution used for internal surface.
‡ Twelve months at locations indicated in columns (2) and (3) and nine additional months at normal room conditions.

Before storage, the chemical durability of bottle A was approximately 18 mgm. of NaOH per liter and that of bottle B was approximately 5.4 mgm.

The results shown in Table IV indicate that the additional nine months of storage at normal room conditions had no significant effect on the nature of the glass surfaces which had been developed during the initial twelve months of storage at the different locations.

Observations were made under ordinary room illumination of the presence of flakes or spicules in the liquid extracts at the conclusion of the tests made after 21 months of storage. The extracts containing low concentrations of alkali showed only small amounts or no flakes, whereas some of the extracts containing high alkali concentrations showed many flakes. No consistent correlation was found, however, between the alkali extraction values and the amounts of flakes observed. Fewer flakes, in general, were observed in the capped bottles. Rinsing, likewise, reduced the number of flakes. The tendency of the weathered bottles to flake during the autoclave test depends on the nature of the weathering products and their adhesion to the glass surface. These properties, in turn, apparently depend on several factors, including the glass composition, the use of a closure during storage, and the storage conditions.

### (3) Composition of Weathering Product

Table V shows the average chemical analyses of the weathering products present on the internal and external surfaces of bottles A, after storage for 12 months at 100°F., 80% relative humidity, and for nine additional months at room conditions. The products were scrubbed from the glass surface while in contact with dilute hydrochloric acid, treated with sulfuric acid, and ignited. The residue was analyzed, and the results were calculated as the oxides on a 100% basis.

TABLE V

COMPOSITION OF WEATHERING PRODUCT FOR BOTTLE A

| Surface | Chemical composition (%): $SiO_2$ | $Na_2O$ | $K_2O$ | CaO | MgO | $Al_2O_3$ | BaO |
|---|---|---|---|---|---|---|---|
| Internal | 39.7 | 39.6 | 2.0 | 10.0 | 3.4 | 2.2 | 3.1 |
| External | 5.1 | 50.9 | 5.7 | 26.2 | 4.7 | 5.4 | 2.0 |

The quantity of sample available was not sufficient for a determination of $B_2O_3$. These analyses, however, show a distinct difference between the compositions of the products on the internal and external surfaces of the bottles. A comparison of the data in Tables I and V indicates that the percentage of silica is considerably lower, whereas those of alkali, lime, alumina, and barium oxide are much higher in the weathering products, as analyzed, than in the original glass.

## V. Experimental Results on Four-Ounce Bottles

### (1) Visual Examination

At the end of 35 and of 56 weeks of storage, all of the bottles were inspected for weathering. Selected samples of capped and uncapped bottles of each type from each storage location were also inspected at frequent intervals during the course of storage. At the end of 35 and of 56 weeks, some of the closures were loose on bottles C, D, E, H, and I stored at (*a*), Table II, and on bottles D, E, F, H, and I stored at (*c*); the closures on the remaining bottles were tight.

No bottles stored at 120°F., 15% relative humidity, or at normal room conditions exhibited distinctly visible weathering during the 13 months of storage. In storage

at 100°F., 80% relative humidity, visible weathering was present on capped and uncapped bottles C, D, E, F, G, and H at the end of 2 weeks, on bottle I at the end of 4 weeks, and on bottle J at the end of 8 weeks. Table VI shows the ranking of the different types of bottles in order of decreasing resistance to weathering (increasing visible weathering) at the end of each of the storage periods indicated at 100°F., 80% relative humidity. (The bracketed bottles showed essentially equal weathering.)

A study of the results given in Table VI was made by means of the rank correlation coefficients calculated by Spearman's formula.[4] A good correlation was considered to be indicated by a coefficient value of at least 0.80, a fair correlation by a value of 0.70 to 0.79, and a poor correlation by a value lower than 0.70.

Although Table VI shows that the rankings were not identical, this study indicated that the rankings of the capped bottles throughout the entire storage period, as well as those of the uncapped bottles, were essentially consistent. Except at the end of 56 weeks, a good correlation was found to exist between the capped and uncapped bottles.

TABLE VI

BOTTLES RANKED BY VISUAL INSPECTION IN ORDER OF DECREASING RESISTANCE TO WEATHERING

| | Weeks of storage at 100°F., 80% relative humidity | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Rank | 2 | 4 | 8 | 12 | 16 | 26 | 35* | 56* |
| | Capped bottles | | | | | | | |
| 1† | J | J | J | J | J | J | J | J |
| 2 | I | H | I | I | I | H | H | D |
| 3 | D | I | D | D | D | I | D | H |
| 4 | H | D | H | H | H | G | I | G |
| 5 | G | C | F | G | G | D | G | I |
| 6 | E | F | G | F | E | C | E | F |
| 7 | C | E | E | E | C | E | C | C |
| 8‡ | F | G | C | C | F | F | F | E |
| | Uncapped bottles | | | | | | | |
| 1† | J | J | J | J | J | J | J | J |
| 2 | I | I | I | I | D | H | H | D |
| 3 | H | H | H | H | I | I | I | E |
| 4 | C | D | D | D | H | G | D | I |
| 5 | D | C | E | G | G | C | G | H |
| 6 | G | E | G | C | C | D | C | C |
| 7 | E | G | C | E | E | F | E | G |
| 8‡ | F | F | F | F | F | E | F | F |

* Examination on all bottles remaining in storage; other examinations on selected samples.
† Best resistance.
‡ Poorest resistance.

## (2) Alkali Extraction Tests

The chemical durability of each bottle type used was measured directly before storage. Determinations were also made at the end of 2, 4, 8, 12, 16, 26, 35, and 56 weeks of storage at conditions (*a*) and (*c*), Table II, and at the end of 35 and of 56 weeks of storage at condition (*f*) of the chemical durability of capped and uncapped bottles of average weathering grade of each type.

The amount of alkali extracted from the internal surface of the bottle by water at 120°C. for one hour was measured by the same method used for the 8-oz. bottles. The results are given in Tables VII, VIII, and IX.

Although chemical durability tests usually include a prior rinsing of the bottles, tests in which no rinsing is employed yield a truer representation of the actual surface conditions produced by weathering. When the bottle was rinsed before the autoclave test, the amount of alkali extracted from the internal surface decreased as expected. This decrease was especially marked in the bottles stored at 100°F., 80% relative humidity, and was least in those stored at 120°F., 15% relative humidity. The slight reduction in alkali extraction produced by rinsing bottles which showed no visible weathering might well be offset by the normal variation,

[4] John F. Kenney, Mathematics of Statistics, Part I, Chapt. VIII. D. Van Nostrand Co., Inc., New York, 1939. 202 pp. + x.

TABLE VII

ALKALI EXTRACTION BY WATER FROM BOTTLES STORED AT 100°F., 80% RELATIVE HUMIDITY

| | Alkali extracted (mgm. of NaOH/liter) | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Storage (weeks) | None | 2 | 4 | 8 | 12 | 16 | 26 | 35 | | 56 | |
| Bottle | Rinsed | Rinsed | Rinsed | Rinsed | Rinsed | Rinsed | Rinsed | Rinsed | Not rinsed | Rinsed | Not rinsed |
| C* | | 24 | 35 | 64 | 70 | 72 | 142 | 149 | 206 | 160 | 191 |
| C | 23.7 | 28 | 27 | 30 | 33 | 40 | 34 | 49 | 56 | 73 | 73 |
| D* | | 24 | 37 | 53 | 56 | 69 | 110 | 176 | 194 | 277 | 258 |
| D | 22.3 | 24 | 28 | 31 | 42 | 40 | 41 | 45 | 57 | 62 | 61 |
| E* | | 25 | 39 | 48 | 45 | 65 | 66 | 109 | 112 | 201 | 177 |
| E | 21.6 | 24 | 37 | 27 | 35 | 40 | 31 | 51 | 64 | 60 | 84 |
| F* | | 26 | 43 | 74 | 80 | 80 | 121 | 149 | 160 | 245 | 267 |
| F | 21.5 | 27 | 34 | 41 | 53 | 64 | 105 | 118 | 123 | 183 | 207 |
| G* | | 15 | 22 | 29 | 34 | 33 | 36 | 42 | 56 | 86 | 91 |
| G | 14.6 | 16 | 28 | 33 | 37 | 40 | 41 | 53 | 67 | 62 | 85 |
| H* | | 15 | 20 | 32 | 38 | 39 | 37 | 61 | 73 | 103 | 106 |
| H | 13.2 | 17 | 19 | 21 | 26 | 27 | 28 | 46 | 54 | 62 | 78 |
| I* | | 14 | 14 | 24 | 24 | 25 | 31 | 31 | 44 | 84 | 129 |
| I | 11.8 | 14 | 14 | 19 | 24 | 24 | 31 | 37 | 51 | 44 | 66 |
| J* | | 9.7 | 11 | 9.8 | 12 | 14 | 11 | 14 | 18 | 19 | 24 |
| J | 8.4 | 10 | 11 | 11 | 12 | 13 | 14 | 19 | 26 | 21 | 27 |

* Capped bottles.

TABLE VIII

ALKALI EXTRACTION BY WATER FROM BOTTLES STORED AT 120°F., 15% RELATIVE HUMIDITY

| Storage (weeks) | Alkali extracted (mgm. of NaOH/liter) | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | None | 2 | 4 | 8 | 12 | 16 | 26 | 35 | | 56 | |
| Bottle | Rinsed | Rinsed | Rinsed | Rinsed | Rinsed | Rinsed | Rinsed | Rinsed | Not rinsed | Rinsed | Not rinsed |
| C* | | 25 | 25 | 23 | 24 | 25 | 26 | 27 | 27 | 27 | 27 |
| C | 23.7 | 26 | 25 | 23 | 25 | 26 | 26 | 27 | 26 | 27 | 28 |
| D* | | 22 | 21 | 20 | 21 | 20 | 21 | 24 | 23 | 23 | 24 |
| D | 22.3 | 22 | 21 | 20 | 22 | 21 | 21 | 23 | 22 | 23 | 26 |
| E* | | 22 | 18 | 22 | 14 | 18 | 23 | 22 | 22 | 23 | 25 |
| E | 21.6 | 22 | 19 | 21 | 6.3 | 21 | 23 | 23 | 22 | 23 | 25 |
| F* | | 22 | 20 | 19 | 21 | 19 | 22 | 23 | 23 | 24 | 25 |
| F | 21.5 | 22 | 20 | 19 | 22 | 19 | 20 | 23 | 18 | 23 | 25 |
| G* | | 15 | 14 | 18 | 14 | 14 | 15 | 16 | 16 | 16 | 18 |
| G | 14.6 | 16 | 14 | 11 | 13 | 13 | 14 | 17 | 15 | 17 | 18 |
| H* | | 15 | 14 | 13 | 14 | 11 | 14 | 14 | 15 | 15 | |
| H | 13.2 | 15 | 13 | 12 | 14 | 12 | 14 | 15 | 14 | 16 | 18 |
| I* | | 13 | 12 | 12 | 11 | 9.5 | 11 | 12 | 13 | 12 | 13 |
| I | 11.8 | 13 | 13 | 12 | 13 | 12 | 12 | 13 | 12 | 13 | 15 |
| J* | | 9.8 | 8.5 | 7.7 | 8.4 | 7.1 | 8.2 | 9.1 | 9.3 | 9.8 | 12 |
| J | 8.4 | 9.0 | 7.5 | 7.8 | 9.2 | 7.8 | 8.3 | 9.4 | 9.7 | 9.8 | 11 |

* Capped bottles.

TABLE IX

ALKALI EXTRACTION BY WATER FROM BOTTLES STORED AT NORMAL ROOM CONDITIONS

| Storage (weeks) | Alkali extracted (mgm. of NaOH/liter) | | | | |
|---|---|---|---|---|---|
| | | 35 | | 56 | |
| Bottle | Not rinsed | Rinsed | Not rinsed | Rinsed | Not rinsed |
| C* | | 26 | 28 | 26 | 29 |
| C | 23.7 | | | 27 | 28 |
| D* | | 23 | 23 | 23 | 27 |
| D | 22.3 | | | 24 | 25 |
| E* | | 24 | 24 | 23 | 26 |
| E | 21.6 | | | 23 | 24 |
| F* | | 24 | 25 | 25 | 28 |
| F | 21.5 | | | 25 | 26 |
| G* | | 17 | 18 | 17 | 19 |
| G | 14.6 | | | 17 | 19 |
| H* | | 15 | 16 | 15 | 17 |
| H | 13.2 | | | 15 | 17 |
| I* | | 13 | 13 | 13 | 15 |
| I | 11.8 | | | 13 | 15 |
| J* | | 9.9 | 10 | 10 | 12 |
| J | 8.4 | | | 10 | 13 |

* Capped bottles.

(after storage) in the chemical durability of different bottles in the same set.

The liquid extracts were examined for the presence of flakes at the conclusion of each chemical durability test. Bottles D, E, and F from room conditions and bottles E and F from 120°F., 15% relative humidity, flaked slightly after storage for 56 weeks; the other bottles stored at these conditions showed no flakes. All bottle types flaked after storage for 56 weeks at 100°F., 80% relative humidity. Initial flaking was noted for bottles C, D, E, and F at the end of 2 weeks, for bottles G and H at the end of 4 weeks, for bottle I at the end of 8 weeks, and for bottle J at the end of 35 weeks of storage at this location.

The flaking of these bottles in the autoclave test paralleled that of the 8-oz. bottles, described previously,

TABLE X

BOTTLES RANKED BY ALKALI EXTRACTION IN ORDER OF DECREASING RESISTANCE TO WEATHERING AT 100°F., 80% RELATIVE HUMIDITY

| Rank | 35 weeks | | 56 weeks | |
|---|---|---|---|---|
| | Capped | Uncapped | Capped | Uncapped |
| 1* | J | J | J | J |
| 2 | I | C | G | D |
| 3 | G | D | H | C |
| 4 | H | I | I | I |
| 5 | E | H | E | E |
| 6 | F | E | C | H |
| 7 | D | G | D | G |
| 8† | C | F | F | F |

* Best resistance.
† Poorest resistance.

except that the tendency of the capped bottles to produce fewer flakes than those uncapped was not so pronounced.

After storage for 56 weeks at 120°F., 15% relative humidity, all bottle types gave somewhat greater alkali-extraction values than initially, but during the course of the storage, all bottle types at times yielded smaller alkali extractions than initially.

Storage for 56 weeks at room conditions increased the alkali-extraction values slightly more than storage at 120°F., 15% relative humidity. Neither of these conditions, during the total storage period used, visibly weathered any of the bottles or produced changes in chemical durability at all comparable with those produced by 100°F., 80% relative humidity.

From the data in Table VII, the bottles may be ranked in order of decreasing resistance to the severe weathering condition of 100°F., 80% relative humidity. Table X shows this ranking at the end of 35 and of 56 weeks for bottles not rinsed before the alkali-extraction test.

The inspection of Tables VII and X shows that, simi-

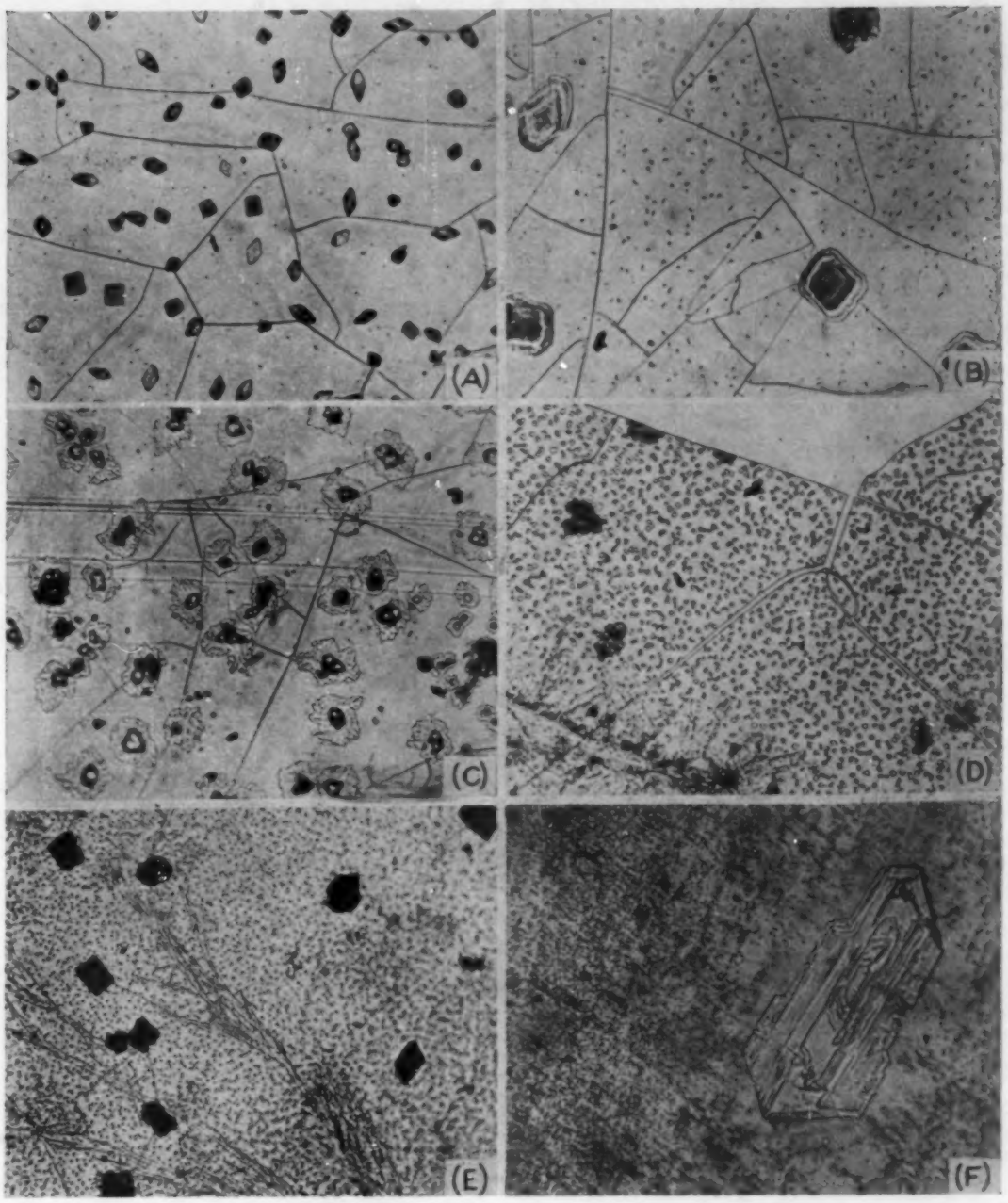


FIG. 2.—(*A*) to (*F*), inclusive; all ×100.

| | Bottle A | Surface | (°F.) | Relative humidity (%) | Storage |
|---|---|---|---|---|---|
| (*A*) | Uncapped | Internal | 100 | 80 | Continuously |
| (*B*) | " | " | " | " | " |
| (*C*) | " | External | " | " | " |
| (*D*) | Capped | Internal | 100 | 80 | Intermittently |
| (*E*) | Uncapped | " | " | " | " |
| (*F*) | " | External | " | " | " |

lar to the results obtained by visual observation, bottle J was the most resistant and bottle F in general was the least resistant to severe weathering conditions.

The rank correlation coefficients indicate that no correlation existed between the capped and uncapped bottles (Table X) but that a good correlation existed between the capped bottles stored for 35 and 56 weeks and also between the corresponding uncapped bottles.

A fairly low correlation was found to exist between rankings made by visual inspection and by the chemical durability test of the bottles subjected to the same length and conditions of storage.

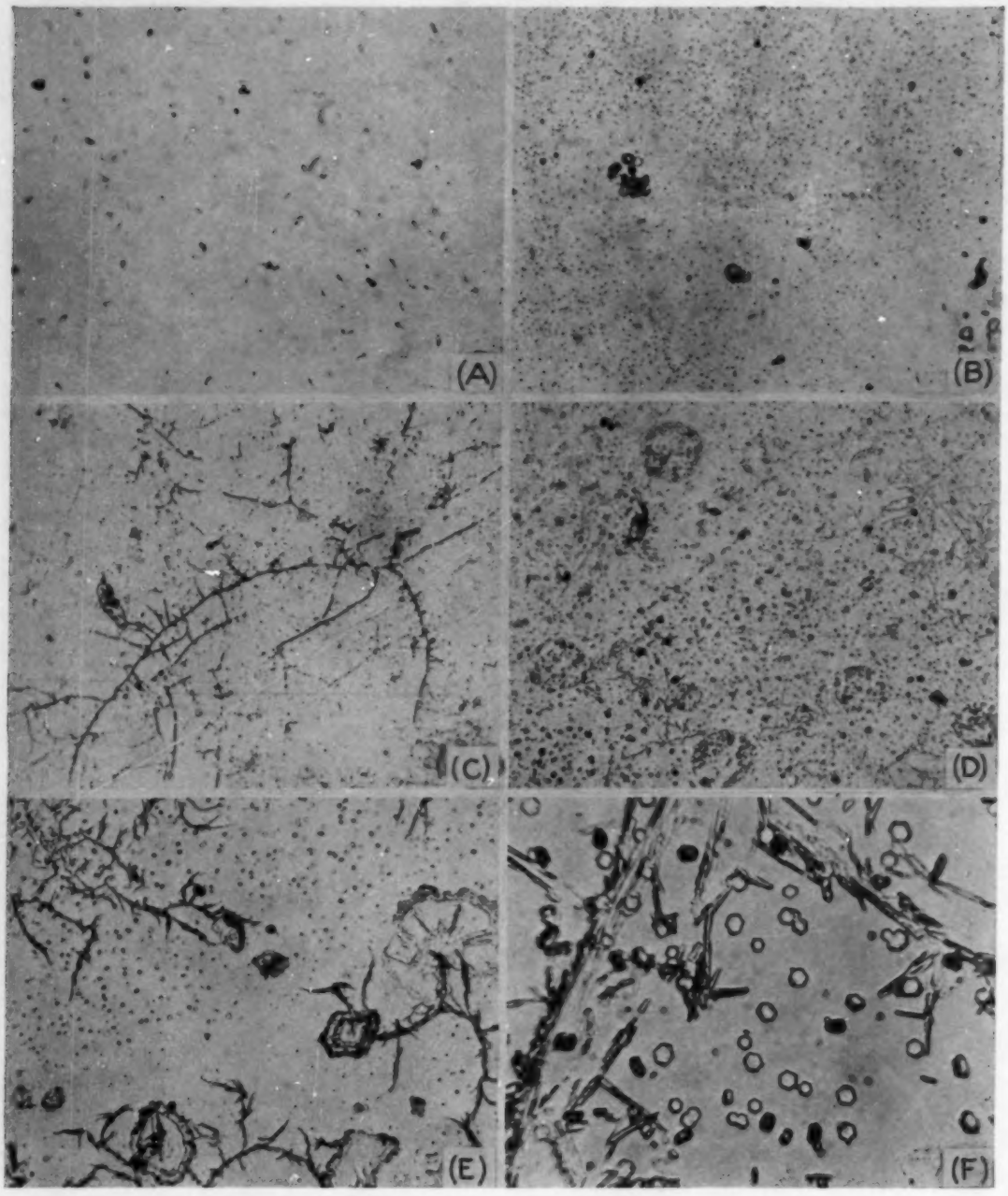


FIG. 3.—(*A*) to (*F*), inclusive; all ×100, except (*F*), which is ×500.

| | Bottle | | Surface | (°F.) | Relative humidity (%) | Storage |
|---|---|---|---|---|---|---|
| (*A*) | Uncapped | A | Internal | 120 | 15 | Continuously |
| (*B*) | " | B | " | 100 | 80 | " |
| (*C*) | Capped | I | External | " | " | " |

| | Bottle | | Surface | (°F.) | Relative humidity (%) | Storage |
|---|---|---|---|---|---|---|
| (*D*) | Capped | F | External | 100 | 80 | Continuously |
| (*E*) | Uncapped | D | Internal | " | " | " |
| (*F*) | Portion of area in (*E*) | | | " | " | " |

## VI. Photomicrographs of Weathered Bottles

The internal and external surfaces of representative, weathered bottles of the different compositions were photographed by transmitted light at a magnification of 100 times to show the structures of the weathering products. Figures 2 through 7 illustrate the typical bottle structures.

Figure 2, (*A*), (*B*), and (*C*), reveals the presence on bottles A, stored at high humidity, of an intact surface film, which is cracked in an irregular manner and is sur-

mounted by crystalline deposits. Figure 2 (*D*) shows the detachment of the film from the glass surface (flake). Calcite, in Fig. 2 (*A*), was found by microscopic examination on the internal and external surfaces of bottles A after storage at 100°F., 80% relative humidity.

The crystals shown in Fig. 2 (*E*) contained both calcium and carbonate, not as calcite but perhaps as aragonite. The large crystal shown in Fig. 2 (*F*) was not positively identified, but it may be described as uniaxial negative with $N_0$ about 1.53. The lowest index in the limited number of samples available was 1.45; this crystal was very soluble in dilute sulfuric acid. Similar crystals were also found on the internal surface of an uncapped bottle D stored at high humidity (see Fig. 6 (*A*)).

Figure 3 (*A*) is typical of bottles A stored at 120°F., 15% relative humidity; insufficient weathering material was visible on the surfaces of the bottles stored at this condition and at normal room conditions to permit a microscopic identification of any crystalline deposit present.

The typical internal surface of capped and uncapped bottles B stored at high humidity is shown in Fig. 3 (*B*); the crystalline material was identified as calcite.

Figure 3, (*C*) and (*D*), exhibits typical structures on the external surfaces, and Figs. 3 (*E*) and (*F*), 4, and 5, (*A*) through (*D*), show structures on the internal surfaces of the 4-oz. bottles after storage at high humidity. Figure 3 (*E*) shows structures in capped and uncapped bottles D, uncapped bottles E, F, and H, and capped bottles G. Figure 3 (*F*), magnified 500 times, shows a portion of the surface illustrated in Fig. 3 (*E*); it also indicates the hexagonal structure of the weathering product, which appears as small circles or dots at a magnification of 100 times.

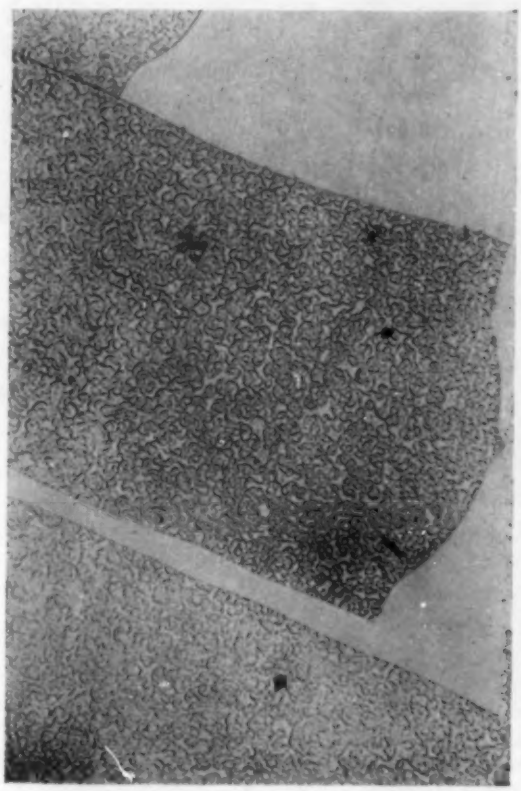

FIG. 4.—Capped bottle F; internal surface; 100°F., 80% relative humidity; ×100.

The structure shown in Fig. 4 for capped bottles F and D, like Fig. 2 (*D*), illustrates the separation of the film, 6.4 $\mu$ thick, from the glass surface. This flaking is accentuated by heat or by mechanical abrasion. After the detachment of the film, the glass surface is perfectly clear, and no such flaking of the external surfaces was found. Microscopic examination in polarized light and treatment with dilute hydrochloric acid at room temperature showed that the material present on the surface film was crystalline and readily soluble, whereas the film itself was amorphous and quite insoluble.

Figure 5 (*A*) shows structures in uncapped bottles D and I, capped bottles G, and both capped and uncapped bottles J. Figure 5 (*B*) is representative of an uncapped bottle C, and Fig. 5 (*C*), of a capped bottle I. The needle crystals on the surface of an uncapped bottle J are apparent in Fig. 5 (*D*); this glass composition was the most resistant to weathering of the 4-oz. bottles.

The slight structure exhibited in Fig. 5 (*E*) is typical of that found on the internal and external surfaces of bottles B stored at 120°F., 15% relative humidity, and of bottles C to J, inclusive, stored at this condition or in a normal room. The structure in Fig. 5 (*F*) was also present on the internal surfaces of bottles C to J stored at normal room conditions.

Figures 6 (*B*) and 7 (*B*), respectively, are duplicate photographs, taken with crossed Nicols, of the areas shown in Figs. 6 (*A*) and 7 (*A*). The birefringence of the weathering products indicates clearly their crystalline nature.*

## VII. Discussion of Results

### (1) Effect of Storage Humidity and Temperature

The most important factor in the weathering conditions used was the relative humidity of the storage atmosphere. Except for bottles B and J, storage for 12 or 13 months at 100°F., 80% relative humidity, produced considerable visible weathering of the bottles tested and greatly decreased their chemical durability (increased the alkali extraction). This storage condition produced a slight visible weathering of the B bottles and a somewhat greater weathering of the J bottles, but it decreased their chemical durability much less than those of the other bottles. Storage at this condition accentuated the flaking of the bottles during subsequent chemical durability tests.

The cyclic storage of bottles A and B at 100°F., 80% relative humidity, and at room conditions was carried out to determine the effect of any "breathing action" that might take place. No significant differences were

* Electron diffraction studies of a few weathered specimens suggest that the weathering products contain hydrated, mixed salts.

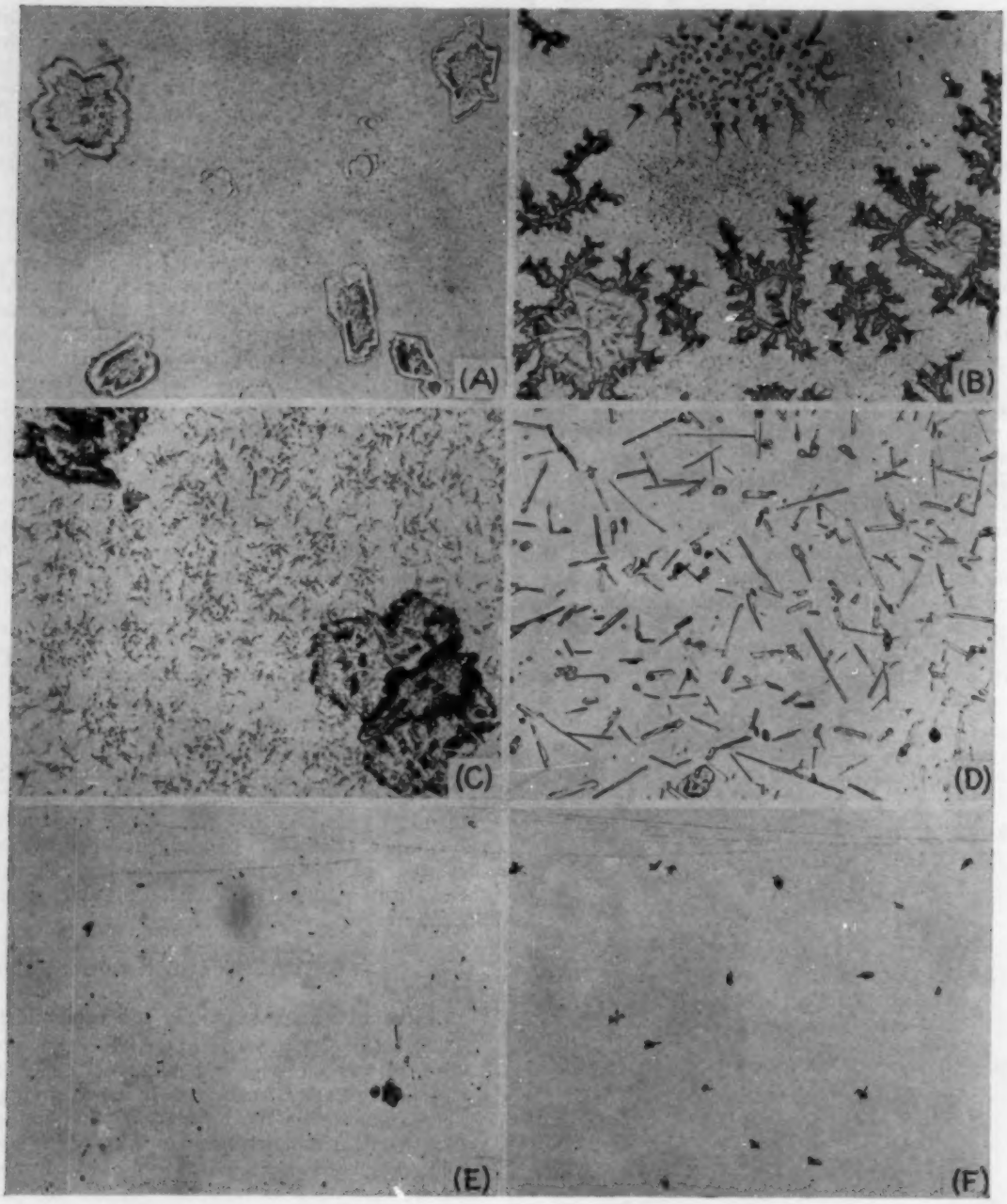


FIG. 5.—(*A*) to (*F*), inclusive; all ×100.

| | Bottle | | Surface | (°F.) | Relative humidity (%) |
|---|---|---|---|---|---|
| (*A*) | Uncapped | I | Internal | 100 | 80 |
| (*B*) | " | C | " | " | " |
| (*C*) | Capped | I | " | " | " |
| (*D*) | Uncapped | J | Internal | 100 | 80 |
| (*E*) | " | H | External | Normal room conditions | |
| (*F*) | " | D | Internal | " | " " |

observed between the weathering experienced by the bottles stored continuously at 100°F., 80% relative humidity, and by those stored at this cyclic condition.

Storage at normal room conditions and at 120°F., 15% relative humidity, produced no visible weathering on any type of bottle tested. These conditions increased the chemical durability of bottles A and B but decreased slightly the chemical durability of the other bottles. The increase in chemical durability was most marked in bottle A stored at 120°F., 15% relative humidity, and it occurred in capped or uncapped bottles, either rinsed or not rinsed before the chemical durability test. Dur-

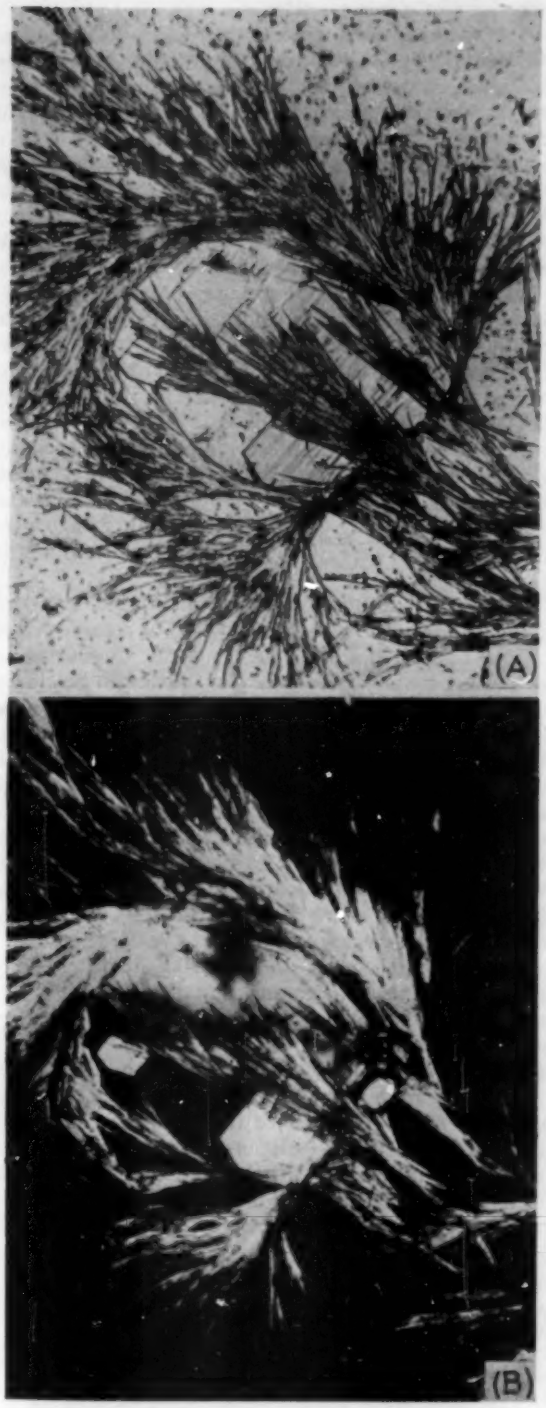


FIG. 6.—(*A*) Uncapped bottle D; internal surface; 100°F., 80% relative humidity, ×100; (*B*) same area as (*A*); crossed Nicols, ×100.

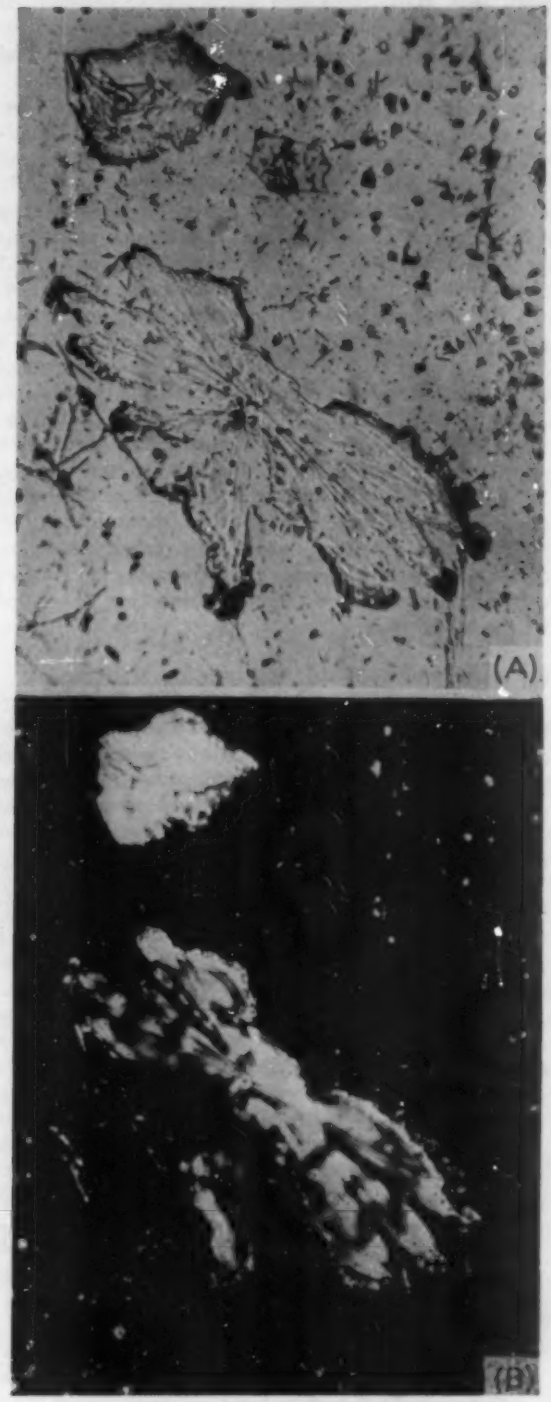


FIG. 7.—(*A*) Uncapped bottle D; internal surface; 100°F., 80% relative humidity; (*B*) same area as (*A*); crossed Nicols, ×100.

ing the course of storage at this condition, all bottles C to J, inclusive, at times showed increased chemical durability. This effect was not nearly so pronounced as in the case of bottle A.

The increase in chemical durability of bottles A and B produced by storage at room conditions was less pronounced but still distinct even on bottles not rinsed before the autoclave test. The chemical durability of bottles C to J, inclusive, was decreased only slightly more by storage at room conditions than by storage at 120°F., 15% relative humidity. The reason for the observed differences in the effect of these two storage conditions on the different sizes of bottles tested is not known, but it may possibly be connected with differences in the conditions of manufacture, in the early histories of the bottles, and in the nature of the actual glass surfaces.

After storage, the internal and external surfaces of the bottles A and B tested were found to be alkaline. Judged by the water-solubility test at 50°C., the external surface was considerably more resistant to severe weathering conditions than was the internal surface. Because the internal surface of the neck of the bottle (see Fig. 1, bottle grades 74 and 135) showed relatively little weathering, the nature of the glass surface produced during the blowing of the container by contact with metal obviously is different from that developed by the blowing air.

### (2) Effect of Capping

Although the capping was done before storage at normal room conditions, a large proportion of the closures on the bottles stored at high humidity became loose and would not have maintained a tight seal against the passage of air and water vapor. This loosening of the closures was due to the absorption of moisture by the molded phenolic caps or by the pulpboard liner backing.

After storage for 12 or 13 months at high humidity, the uncapped bottles (except bottles A, C, E, and I) were slightly more visibly weathered than the capped. During the first six months of storage under this condition, the chemical durability of the capped bottles C, D, E, F, and H was lower and that of bottle G was higher than the values found for the uncapped bottles. Capping had no significant effect on the durability of bottles I and J. At the end of 12 or 13 months, the chemical durability of the capped bottles (except B and J) was lower than that of the uncapped. No definite relation between capping and visible weathering or chemical durability was found to hold for all the bottle compositions throughout the storage period.

Capping had no appreciable effect on the visible weathering or on the chemical durability of the bottles stored under the other two conditions.

### (3) Effect of Glass Composition

The resistance to severe weathering conditions depends to a large degree on the glass composition. The data indicate that bottle B was slightly more resistant than bottle J to severe weathering conditions, and it was considerably more resistant than the remaining bottles. Based on the amounts of alkali extracted per unit of internal surface area in the autoclave tests made before storage, bottle B initially was slightly superior in chemical durability to bottle J and was considerably superior to the other bottles.

The data obtained indicate that the initial chemical durability values obtained before storage arrange the bottles in classes of resistance to weathering, but they may not arrange the individual members of each class in their order of weathering resistance.

On the basis of the different tests used to determine the amount of weathering, of the 8-oz. bottles, B was far more resistant to severe weathering conditions than A; of the 4-oz. bottles, J was the most resistant and F was the least resistant to severe weathering conditions.

Although marked differences in resistance to weathering were found among the compositions used, no simple relationship was obtained between the chemical composition and the weathering, even for any given condition of storage. The relative resistances of the different bottle compositions tested depend on several factors, which include (*a*) the chemical composition of the glass, (*b*) capping, (*c*) the length, humidity, and temperature of storage, (*d*) the method employed to determine the degree of weathering, and (*e*) possibly other factors influenced by the conditions of manufacture and of the glass surfaces.

The results indicate that the conditions and length of storage and the method of test should be considered for an accurate evaluation of the resistance to weathering of a given container composition. Although bottles of distinctly different resistances to weathering may be identified, in general, either by visual or chemical tests, the rankings of a number of different bottle compositions by means of these two methods may not wholly agree because of the different properties measured. The usual chemical tests determine only the amount of weathering product leached from the glass surface as total weight or as alkali by titration, whereas visual inspection yields a qualitative measure of the optical density of the weathering product.

Factors were calculated for the constituent oxides of the glass on the assumption that the weathering, as measured by the chemical durability test, might be an additive property of these components expressed in molar percentages. The use of these factors arranges the tested bottle compositions approximately in the observed order of resistance to the weathering condition selected for the calculation. The factors, however, are not quantitatively accurate for all of the bottle compositions used. These results, as well as those obtained by the consideration of other simple relationships between the glass composition and the weathering, indicate that any relation which may exist between the chemical composition and the weathering experienced under any given condition is probably complex.

## VIII. Conclusions

(1) Important factors have been obtained on the effect of storage, under diverse conditions, on the appearance of the surface and the chemical durability of ten commercial flint-glass compositions.

(2) The atmospheric humidity is the most important factor in the storage conditions used.

(3) The weathering produced depends on several factors, including the chemical composition of the glass; the length, humidity, and temperature of storage; the use of a closure during storage; and the nature of the glass surface developed during the manufacture of the container. All of these factors (except the chemical composition) as well as the method of measurement of the weathering should be taken into account for an accurate evaluation of the resistance to weathering of a given container composition.

Although several factors are operative in weathering, the severe weathering effect of high humidity may be controlled by means of the chemical composition of the glass.

The photomicrographs of the weathered glass surfaces show the presence of crystalline deposits and of a surface layer, segments of which may become detached as flakes. A portion of the deposits was identified as calcite.

**Acknowledgment**

The authors take pleasure in acknowledging the valuable assistance given in different portions of the work by members of the laboratory staff. They are especially indebted to J. H. Widmyer for the photomicrographic work, K. C. Lyon for the microscopic identification of the crystalline weathering products, J. L. Hess for the chemical analyses and R. W. Merley for experimental assistance.

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# OXIDATION-REDUCTION EQUILIBRIA IN GLASS BETWEEN IRON AND SELENIUM IN SEVERAL FURNACE ATMOSPHERES*

By Frank Day, Jr.,† and Alexander Silverman

Abstract

This study has been limited to the reactions between iron and selenium in soda-lime and potash-soda-lime glasses melted in atmospheres of air, nitrogen, and carbon monoxide. Glasses containing selenium and iron, together and singly, were melted in the several atmospheres, and their spectral absorption curves between 350 and 1000 mμ were obtained.

An analysis of these curves shows that under neutral or slightly oxidizing conditions selenites react with ferrous iron as follows:

$$Na_2SeO_3 + 4FeO \rightleftarrows Se^0 + 2Fe_2O_3 + Na_2O.$$

This reaction leads to an increase in red and brown and a decrease in blue colors. The decolorizing action of selenium may be explained by this reaction because the colorless selenite ion oxidizes the more colored ferrous ion to the less colored ferric ion, and the increase in the red elemental selenium color physically compensates as a complimentary color for the remaining unoxidized ferrous ion. The results show that it is not necessary to postulate the formation of ferrous selenide to explain the color changes.

The results also show that under reducing conditions the principal reaction is

$$xSe^0 + 2FeO + Na_2O \rightleftarrows Na_2Se_x + Fe_2O_3.$$

## I. Introduction

When selenium is incorporated in a glass batch, without sulfur and cadmium, and the glass is melted under slightly oxidizing conditions, a pink color is obtained. If the melting conditions are reducing, the glass is brown. The green color also decreases when small amounts of selenium are added to a glass containing iron. This reaction at first was attributed exclusively to physical compensation of the green iron color by the complimentary pink selenium color and later to the formation of an iron selenium compound.

The purpose of the present work is to show that the decolorizing action of selenium is due to a simple oxidation-reduction reaction. The effect of the furnace atmosphere on this reaction has also been studied.

### (1) Review of Literature

All of the problems of color changes in selenium glasses, of selenium decolorizing, and of decolorizing in general are related. The literature on this subject is voluminous; an extensive review, however, will be superfluous inasmuch as bibliographies are available, notably in papers by Gooding and Murgatroyd[1] and, to a lesser extent, by Jaeckel[2] and Kühl, Rudow, and Weyl.[3] Only the more recent papers that have a direct bearing on the problem will be discussed in this review.

* Presented in part under the title "Chemical Mechanism of Decolorizing Glass with Selenium" at the Autumn Meeting of the Glass Division, The American Ceramic Society, Conneaut Lake Park, Pa., September 13, 1941.

Contribution No. 439 from the Department of Chemistry, University of Pittsburgh, Pittsburgh, Pa.

† Submitted to the Graduate School of the University of Pittsburgh in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[1] (*a*) E. J. Gooding and J. B. Murgatroyd, "Investigation of Selenium Decolorizing," *Jour. Soc. Glass Tech.*, **19** [73] 43–103 (1935); *Ceram. Abs.*, **14** [9] 215 (1935).

(*b*) E. J. Gooding, "Decolorizing of Glass, Review," *Jour. Soc. Glass Tech.*, **20** [81] 375–83 (1936); *Ceram. Abs.*, **17** [1] 11 (1938).

[2] Georg Jaeckel, "Das Entfarben des Glasses" ("Decolorization of Glasses"), *Glastech. Ber.*, **8** [5] 257–65 (1930); *Ceram. Abs.*, **10** [5] 334 (1931).

[3] C. Kühl, H. Rudow, and W. Weyl, "Oxydations- und Reductionsgleichgewichte in Farbgläsern," ("Oxidation and Reduction Equilibria in Colored Glasses"), *Sprechsaal*, **71** [7] 91–93; [8] 104–106; [9] 117–18 (1938); *Ceram. Abs.*, **18** [1] 18 (1939).

Höfler[4] has made one of the most significant contributions to the solution of the problem of color changes in selenium glasses. He studied the influence on color of the furnace atmosphere, the form in which the selenium is added, melting temperature and time, selenium concentration, stirring, additions of oxidizing and reducing agents, speed of cooling, and various base glass compositions. He states that a glass made under extreme reducing conditions in an atmosphere of hydrogen is colorless to brown; in a slightly reducing atmosphere, it is brown; in a neutral atmosphere, pink; and in an oxidizing atmosphere, pink to colorless. An increase in the melting time and stirring accentuates these colors. Additions of oxidizing agents, such as $NaNO_3$ and $As_2O_3$, and of reducing agents, such as carbon and aluminum, produce effects analogous to those of the corresponding atmospheres; they also react more rapidly, but their effects can be overcome by longer melting in a controlled atmosphere.

Höfler's work clearly demonstrates that there are four recognizable oxidation-reduction states in selenium glasses, namely, (1) a reduced colorless state, (2) a less reduced brown state, (3) a neutral and slightly oxidized pink state, and (4) a strongly oxidized colorless state. Selenide solutions are colorless; polyselenide, brown; selenium vapor may be red; and the selenites and selenates are colorless, which led him to postulate that the colors in glass correspond to these states and that the mechanism of color change, therefore, may be attributed to reaction (1).

$$\underset{\text{(colorless)}}{Se^{=}} \rightleftarrows \underset{\text{(brown)}}{Se_x^{=}} \rightleftarrows \underset{\text{(red)}}{Se^0} \rightleftarrows SeO_3^{=} \rightleftarrows \underset{\text{(colorless)}}{SeO_4^{=}} \qquad \text{Reduction} \longleftarrow \quad \text{oxidation} \longrightarrow \qquad (1)$$

Höfler also found that the form in which the selenium is added concurs with this mechanism. If, for instance, the selenium is added as $Na_2SeO_4$ and melted under reducing conditions, a longer melting time is required to produce a brown color than when selenium is added as the element. Higher temperatures, furthermore, accelerate the reaction rate, and an increase in the alkalinity favors the formation of the brown reduced forms. The substitution of $Na_2O$ for $K_2O$ produces a slightly more yellowish glass, but selenium in soda glasses reacts in the same manner as in potash glasses.

Among the more recent studies on selenium decolorizing is that of Höfler and Dietzel.[5] In addition to their work on striking, they found that if a blue-green iron glass containing 0.10% of $Fe_2O_3$ is superimposed on a second iron-free glass containing a few thousandths of 1% of selenium, the resulting couple is neutral gray owing to the physical compensation of the green iron color by the complimentary pink of the selenium. When these glasses are melted together, the resulting glass is decidedly red-brown. They also demonstrated this phenomenon quantitatively by spectral transmittancy curves covering the range between 450 and 700 mμ; for example, $(I/I_0)$ for a glass that contains 0.1% of $Fe_2O_3$ multiplied by $(I/I_0)$ for a glass to which 0.01% of Se has been added does not produce $(I/I_0)$ for a glass containing both 0.1% of $Fe_2O_3$ and 0.01% of Se. These quantities, according to Beer's law, should be equal when a mixture occurs. Höfler and Dietzel correctly interpret this inequality to be the result of a reaction between iron and selenium; by reasoning on the basis of the analogy to the reaction between ferrous and sulfide ions to precipitate ferrous sulfide, they postulate the formation of ferrous selenide to which they assign a red color as follows:

$$\underset{\text{(blue)}}{FeO} + Na_2Se \rightleftarrows \underset{\text{(red)}}{FeSe} + Na_2O \qquad (2)$$

As additional evidence for this reaction, they point out that ferrous selenide results from an association of ions and that most striking reactions, such as are encountered in ruby glasses, are due to association. It is well known that selenium-decolorized glasses may strike during annealing. This striking to produce a more intense pink color is also favored by reducing melting conditions which, in turn, would favor the formation of the more reduced $Na_2Se$ and FeO; this formation, by mass action, would then produce more FeSe.

Gooding and Murgatroyd[6] have verified the fact that a reaction occurs between iron and selenium in glass. They found that high temperatures produce blue colors in glasses which contain iron, and they attribute this color to reaction (3).

$$2Fe_2O_3 \underset{\text{low } T}{\overset{\text{high } T}{\rightleftharpoons}} 4FeO + O_2 \qquad (3)$$

Selenium glasses, containing oxidizing agents, moreover, retain the bulk of their selenium as $SeO_2$, and as the temperature increases and as oxidizing agents are removed, elemental selenium is produced (reaction (4)).

$$SeO_2 \rightleftarrows Se + O_2 \qquad (4)$$

They also made a quantitative determination of the color of these glasses with a Lovibond tintometer. When both selenium and iron are present, they found that the color is not the same as that obtained if the color of a glass containing iron alone were combined with the color of a glass containing only selenium. There is instead a decrease in blue and an increase in red and yellow, which means that a reaction has occurred. Gooding and Murgatroyd ascribe reaction (5) to the formation of ferrous selenide.

$$\underset{\text{(red)}}{2Se} + \underset{\text{(blue)}}{Fe_3O_4} \rightleftarrows \underset{\text{(yellow-brown)}}{2FeSe} + \underset{\text{(brown)}}{2Fe_2O_3} + O_2 \qquad (5)$$

They also attribute the decrease in blue color, when

[4] W. Höfler, "Verhalten des Selens im Glase," ("Selenium in Glass"), *Glastech. Ber.*, **12** [4] 117–34 (1934); *Ceram. Abs.*, **14** [4] 90 (1935); English translation by S. R. Scholes, "Behavior of Selenium in Glass," *Glass Ind.*, **15** [6] 122–25 (1934).

[5] (*a*) W. Höfler and A. Dietzel, "Die Verfärbung von Selengläsern im Kühlofen" ("Selenium Glass in Annealing Oven"), *Glastech. Ber.*, **12** [9] 301–302 (1934); *Ceram. Abs.*, **14** [2] 36 (1935).

(*b*) W. Höfler and A. Dietzel, "Das Anlaufen der Seleneisengläser und seine Bedeutung für die Entfärbung mit Selen" ("Warming in of Selenium-Iron Glasses and Significance in Decolorizing with Se"), *Glastech. Ber.*, **14** [11] 411–21 (1936); *Ceram. Abs.*, **18** [1] 18 (1939).

(*c*) A. Dietzel, "Theory of Decolorizing with Selenium," *Jour. Soc. Glass Tech.*, **21** [83] 87–94 (1937); *Ceram. Abs.*, **17** [8] 276 (1938).

arsenic is added to an iron-containing glass, to reaction (6).

$$\underset{\text{(blue)}}{Fe_3O_4} + As_2O_3 \rightleftarrows \underset{\text{(colorless)}}{FeAs_2O_4} + \underset{\text{(brown)}}{Fe_2O_3} \qquad (6)$$

In their selenium melts, the addition of arsenic causes a decrease in pink color, which they assign to a reaction, but they do not specify what it is. They suggest, however, that it may be due to the formation of a colorless selenium-arsenic compound.

## II. Experimental Work

The present work has been limited to a study of the effect of iron and selenium in glasses which were synthesized to have a molecular composition of $K_2O{\cdot}Na_2O{\cdot}2CaO{\cdot}9SiO_2$ and $2Na_2O{\cdot}2CaO{\cdot}9SiO_2$. One series of soda-lime glasses was melted in air, and the three series of potash-soda-lime glasses were melted in air, nitrogen 99.2%, and carbon monoxide 97.3%, respectively. Each series consisted of four kinds of glasses with frequent duplicates as follows: (1) with no colorants, (2) with 2 parts of ferric oxide per 1000 parts of silica, (3) with 5 parts of selenium per 1000 parts of silica, and (4) with 2 parts of ferric oxide and 5 parts of selenium per 1000 parts of silica.

Table I shows the percentage composition of these two base glasses.

TABLE I

BASE GLASSES (COMPOSITION %)

| | Type of glass | |
|---|---|---|
| Oxide | $K_2O{\cdot}Na_2O{\cdot}2CaO{\cdot}9SiO_2$ (%) | $2Na_2O{\cdot}2CaO{\cdot}9SiO_2$ (%) |
| $SiO_2$ | 66.8 | 69.6 |
| CaO | 13.9 | 14.4 |
| $Na_2O$ | 7.7 | 16.0 |
| $K_2O$ | 11.6 | |

The percentage of ferric oxide added was 0.133 in the potash glass and 0.139 in the soda glass. The percentage of selenium retained in the glass after melting, which was determined by the method of Pavlish and Silverthorn,[6] was 0.080%. This value, with a probable error of ±0.003% for each glass, was found for all glasses regardless of the atmosphere in which they were melted and whether or not iron was present.

The raw materials, c.p. sodium carbonate, potassium carbonate, and calcium carbonate, were analyzed and were found to conform to American Chemical Society specifications.[7] The ferric oxide and the elemental selenium, which were precipitated, were found to be pure by analysis. The silica was a pulverized, acid-washed sand which contained 99.85% of $SiO_2$, 0.14% of $Al_2O_3$, and less than 0.005% of $Fe_2O_3$. The dried carbonates and ignited sand, in quantities sufficient to prepare 26.963 gm. of potash-soda glass or 25.890 gm. of soda glass, were weighed out accurately to the nearest milligram, and the dried selenium and ferric oxide were weighed to the nearest 0.1 mgm. These materials were mixed thoroughly and transferred to a cylindrical, unglazed porcelain crucible (see Fig. 1). The crucible and batch were placed in an electric muffle, slowly heated to 830°C. to evolve the bulk of the carbon dioxide, cooled in a desiccator, and stored there prior to melting. All of the glasses of any one series, and in some cases of several series, were given this sintering treatment at the same time.

An Ajax-Northrup electrical induction furnace was used for melting (Fig. 1). It was held within ±12°C. of the desired temperature by an on-off control actuated by a Leeds and Northrup Micromax controller whose primary element is a platinum-platinum 10% rhodium thermocouple. This particular setup was used for melting in an atmosphere of nitrogen or of carbon monoxide. The melts conducted in air were made with the thermocouple and crucible in the position shown in Fig. 1, but with a short 12-in. outside porcelain tube which was flush with the top of the furnace. This tube was loosely covered to allow circulation of air during melting.

The furnace was heated rapidly to 1200°C., the crucible was slowly lowered into the melting compartment, and the furnace was rapidly heated to 1500°C.

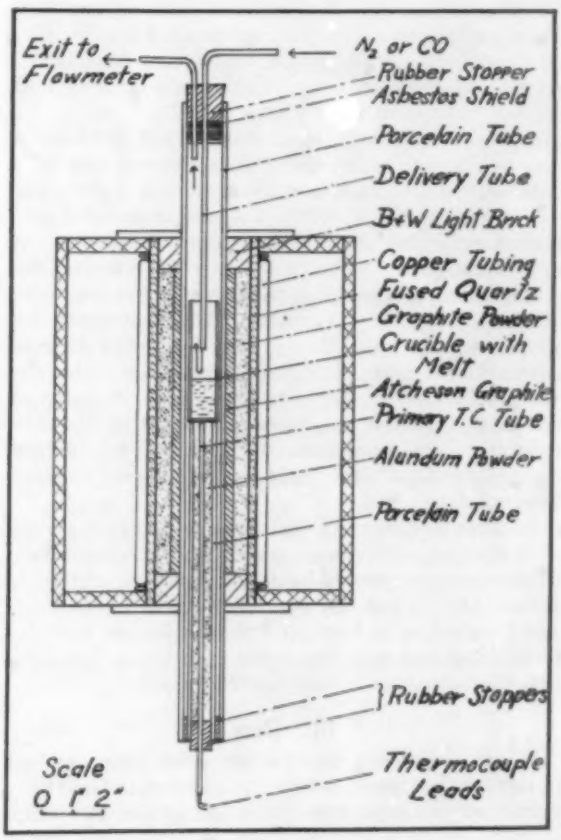


FIG. 1.—Melting apparatus.

[6] A. E. Pavlish and R. W. Silverthorn, "Analysis of Selenium in Glass," *Jour. Amer. Ceram. Soc.*, **23** [4] 116–18 (1940).

[7] "A. C. S. Analytical Reagents, Specifications Recommended by Committee on Analytical Reagents of the American Chemical Society," American Chemical Society, Washington, D. C., March, 1941.

The excess selenium in the melts was evolved as a red-gray smoke at about 1350°C. After the crucible had been in the furnace for 15 minutes, the glass was stirred, the furnace was covered or stoppered, and $N_2$ or CO was passed over the melt at a rate of 150 ml. per minute. The furnace was then unstoppered, and the glass was stirred four times at 15-minute intervals. This procedure gave a total melting time of $1^1/_4$ hours, of which 1 hour was under controlled atmosphere.

Fifteen minutes after the final stirring, the melt was poured into a mold, cooled rapidly to room temperature, and the glass was removed from the mold. After one or two series of glasses had been prepared, they were all annealed together, ground, and polished to form specimens with flat parallel sides. All specimens of any one series were ground to the same thickness (±0.01 mm.), but not all series were alike; for example, all of the straight soda glasses were 7.18 mm. thick; the potash-soda glasses melted in air were 5.04 mm., and the potash-soda glasses melted in $N_2$ and CO were 5.55 mm.

Later in the calculations, all of the extinction values were corrected to a thickness of 1 cm., that is, specimens of the same thickness, which are always encountered in one series, are strictly comparable according to the Lambert law. There can thus be no discrepancies due to unequal thickness in a given series; small errors occur, however, owing to deviations from the Lambert law when a glass from one series of a certain thickness is compared with a glass from another series of another thickness. In the latter case, the results must be accepted with the reservation that a slight error may be present.

The spectral transmittancies were determined with a Coleman spectrophotometer* in conjunction with a Coleman electrometer; a 7.5-mμ slit was used. The spectrophotometer was adjusted so that errors due to surface reflection and absorption by the base glass were eliminated. This was done by passing the standard, or $I_0$, beam through an iron-free or selenium-free specimen and then setting the instrument for 100% transmission. The specimen containing the iron, selenium, or both was then introduced into the standardized beam, and the decrease in intensity at the particular wave length was measured by the electrometer. This procedure, theoretically, should yield the transmittancy curve only for the coloring material in solution.

In order to compare the absorption curves of glasses with aqueous solutions containing known colored ions, dilute and concentrated solutions of ferrous and ferric sulfate and a polyselenide solution were prepared. The transmittancy curves for these solutions were determined in matched, flat-walled cuvettes as containers in the same manner as those for the glasses.

## III. Data

The transmittancy data for the potash glasses melted in nitrogen are given in Fig. 2. These data have been converted into extinction values (see section IV) which

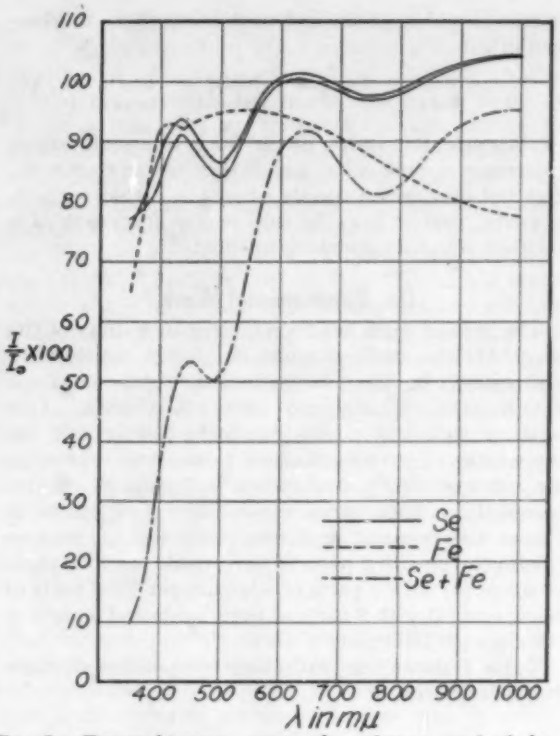


FIG. 2.—Transmittancy curves for glasses melted in nitrogen.

are more convenient for interpretation. Transmittancy curves for all of the glasses, therefore, are not presented here. Those given are similar to the curves obtained for other series except for the glasses melted in carbon monoxide. The double curves indicate the degree of reproducibility that may be expected for two different specimens.

## IV. Treatment of Data

### (1) Preliminary Examination

A combination of the Beer and Lambert laws may be stated mathematically as follows:

$$E = \log(I_0/I) = klc.$$

$E$ = extinction.
$I_0$ = intensity of light beam striking first surface of absorbing body.
$I$ = intensity of beam emerging from second surface.
$l$ = thickness of specimen.
$c$ = concentration of absorbing material in specimen.
$k$ = specific extinction.

If the transmittancies, $(I/I_0) \times 100$, for various wave lengths are divided by 100 and their negative logs taken, the extinction values, which are proportional to the product of thickness and concentration, may be obtained. An extinction curve occurs when a series of these values for a particular specimen is plotted against the appropriate wave lengths. If the specimen is an absorbing type, a peak (or peaks) will be obtained in the curve, and their wave-length positions are characteristic of the absorbing substance. If the concentration of the specimen is changed, the wave-length

* Coleman D. M. spectrophotometer, Model 10-S.

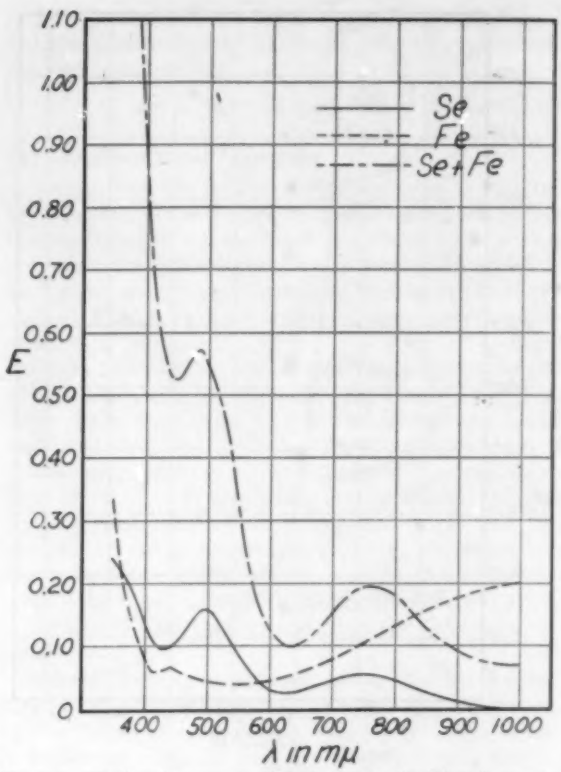


FIG. 3.—Extinction curves for glasses melted in nitrogen.

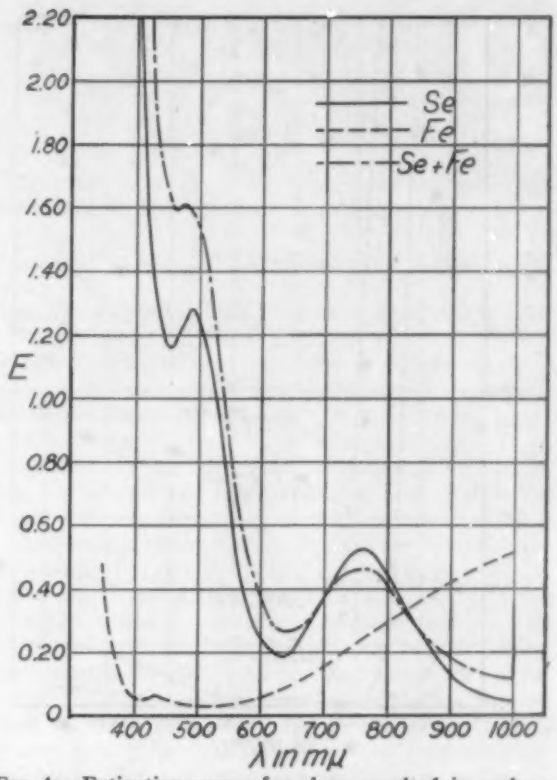


FIG. 4.—Extinction curves for glasses melted in carbon monoxide.

positions of these peaks are not appreciably shifted, but the extinction values increase by an amount proportional to the increase in concentration when the thickness of the specimen is constant. When more than one absorbing substance is present in the specimen, the extinction value at any one wave length is the sum of the extinction values of each substance at that wave length.

A useful application of extinction curves arises from the fact that similar curves are obtained for the same solute in solvents having approximately the same electrical properties; the extinction curve for the tetracoordinated cobalt ion in water is similar to that obtained for this ion in glass. Comparison of the shape and approximate peak position of an ion in aqueous solution with an ion in glass may thus lead to information concerning the ion in the glass.

The transmittancy data of the type given in Fig. 2 were converted into extinction values which yield curves similar to those shown in Figs. 3 and 4. These curves, however, are not calculated directly from the data but represent corrected values. This correction and its explanation are discussed in section IV (2). The correction is small and has little influence on the peaks and on the relative positions of the extinction curves. These curves, therefore, may be used to demonstrate the significance of the data.

Extinction curves for dilute and concentrated ferrous and ferric sulfate solutions and a polyselenide solution, all calculated directly from the transmittancy data, are given in Figs. 5 and 6 for comparison purposes.

(1942)

Höfler's work on selenium pink glasses[4] shows that a pink color is obtained when selenium is introduced into a batch, which is melted under neutral or slightly oxidizing conditions. This pink form of elemental selenium is in equilibrium with other colorless ions, and the predominating equilibrium, according to Höfler, is reaction (7).

$$\underset{\text{(red)}}{Se^0} \rightleftarrows \underset{\text{(colorless)}}{SeO_3^{=}} \rightleftarrows SeO_4^{=} \qquad (7)$$

This elemental selenium is responsible for a curve with two absorption bands, which is shown by curves in Figs. 3 and 4 for glasses that contain selenium alone.

Inspection of the iron-glass curve in Fig. 3 shows part of an absorption band in the near infrared and the beginning of a sharp cutoff in the near ultraviolet. A comparison of this curve with those in Fig. 5 shows that the absorption at the longer wave lengths is due to ferrous ions; at the shorter wave lengths, it is caused primarily by ferric ions. This means that iron in glass is present in both the ferrous and ferric forms and that a melting equilibrium is established such as reaction (8).

$$Fe^{+++} \rightleftarrows Fe^{++} \qquad (8)$$

Comparison of the extinction values for the iron glass curves at 1000 mμ in Figs. 3 and 4 shows that the extinction value has increased for the glass melted in carbon monoxide. This means that reducing conditions shift equilibrium (8) to the right, which favors the for-

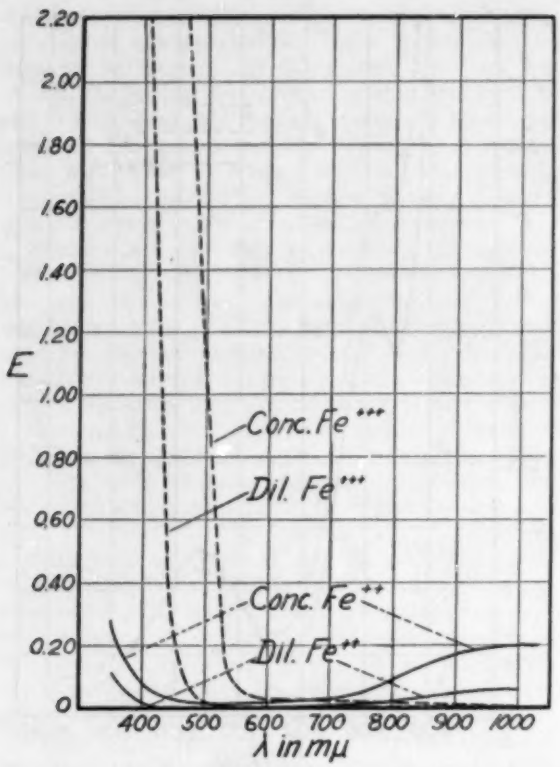


FIG. 5.—Extinction curves for ferrous and ferric iron solutions.

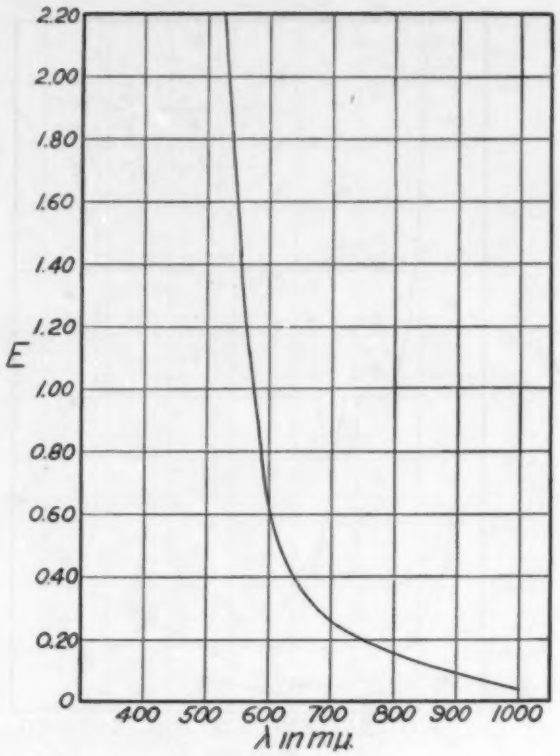


FIG. 6.—Extinction curves for an aqueous polyselenide solution.

mation of the blue ferrous ion (this fact has been known for some time).

When selenium and iron are introduced together into the same glass, the resulting extinction curve is not the same as one calculated by adding the extinction values of the iron and selenium alone. For instance, the sum of the individual constituents at 1000 mμ is 0.20, but when both are present in the same glass, the value decreases to 0.07; at 500 mμ, the sum is 0.205, and the value for both melted together, 0.575. The sum at shorter wave lengths, in general, is much less; at longer wave lengths, it is much greater. This can only mean that a reaction has occurred between iron and selenium when they are melted together, which agrees with the work of Höfler and Dietzel,[5] and that of Gooding and Murgatroyd.[1(a)]

Close inspection of the absorption maxima (Fig. 3) at 760 mμ for both glasses containing selenium shows that the wave-length position is the same regardless of the iron but that the extinction value, in the presence of iron, has increased. The kind of material, therefore, producing the pink color has not changed from the reaction, but it has a greater concentration. This material, according to Höfler,[4] is elemental selenium, which shows that equilibrium (9) has been shifted to the right in the presence of iron.

$$\underset{\text{(colorless)}}{SeO_3^{=}} \rightleftarrows \underset{\text{(red)}}{Se^0} \qquad (9)$$

This conclusion does not agree with those of Höfler and Dietzel[5] and of Gooding and Murgatroyd,[1] who have postulated the formation of ferrous selenide to account for the increase in color in t' e presence of iron.

Figure 3 also shows that the extinction value at 1000 mμ is less for glasses containing iron and selenium than it is for those that contain iron alone. Inasmuch as the absorption band at this point has been shown to be due to ferrous ion and as extinction is proportional to concentration, it must be concluded that the selenium is causing the concentration of ferrous ions to decrease, converting them to something else which is represented here by $X$ because the identity has not been established at this stage. In other words, reaction (10) is shifted to the right.

$$Fe^{++} \rightleftarrows X \qquad (10)$$

When reactions (9) and (10) are added together, the result is reaction (11).

$$SeO_3^{=} + Fe^{++} \rightleftarrows Se^0 + X \qquad (11)$$

The selenite obviously has acted as an oxidizing agent, and the ferrous ions, which have disappeared, must have gone to the oxidized form, namely ferric ions. Figure 3, furthermore, shows a sharp increase at the shorter wave lengths for glasses containing both iron and selenium. This wave-length position occurs where both ferric and polyselenide ions absorb (see Figs. 5 and 6); $X$, therefore may be $Fe^{+++}$, and when both iron and selenium are present in glass, reaction (12) occurs.

$$SeO_3^{=} + Fe^{++} \rightleftarrows Se^0 + Fe^{+++} \qquad (12)$$

The increase in absorption at the shorter wave lengths, moreover, may be due in part to the polyselenide ion of reaction (13).

$$Se^0 + Fe^{++} \rightleftarrows Se_2^- + Fe^{+++} \qquad (13)$$

## (2) Mathematical Treatment

To establish the indicated reaction more thoroughly by removing from the selenium-plus-iron glass curves the contribution of increased selenium, thus leaving only the curves due to iron and polyselenide, the data were given a simple mathematical treatment in accordance with the laws of colorimetry and chemical equilibrium.

Figure 2 shows that the transmittancy curves for the glasses containing selenium alone rise above 100% at longer wave lengths. This rise is abnormal and would mean literally that there is less than zero concentration of absorbing material, which is a physical impossibility. The rise, in reality, may mean several things, namely, (1) that selenium may have fluoresced or (2) that the base or solvent glass, exclusive of the selenium color effect, for some special reason may have transmitted more light than it would without selenium when the $I_0$ (standard) beam was passed while the data were being obtained.

Because there is no apparent reason for attributing the effect to fluorescence and because a possible reason for the second case does exist, the latter is taken as the probable one, and the data are corrected accordingly. When selenium is added to a glass, it acts as a refining agent, removing seeds and producing a more homogeneous glass. In the glasses from which these data were taken, the selenium acted in this manner, whereas glasses containing iron alone or no colorants were more cordy and contained a few seeds. These defects produce light-scattering errors. To correct for these errors, selenium was assumed, in this respect, to have an equal effect on all of the glasses to which it was added; furthermore, because the scattering is slight, the correction to be applied was assumed to be the same at all wave lengths, inasmuch as the shorter wave lengths are scattered only slightly more than the longer wave lengths. To calculate this correction, transmission data for glasses containing only selenium melted in both $N_2$ and CO were taken at the longer wave lengths in which the only coloring material is red $Se^0$. When a selenium glass is melted in a CO atmosphere, an increase in $Se^0$ occurs, according to reaction (14).

$$SeO_3^- + CO \rightleftarrows Se^0 + CO_2 \qquad (14)$$

This increase in $Se^0$ must be taken into account as follows:

$T_1$ = $(I/I_0)$ at $\lambda_1$ for glass melted in $N_2$.
$T_2$ = " " $\lambda_1$ " " " " CO.
$T_1'$ = " " $\lambda_2$ " " " " $N_2$.
$T_2'$ = " " $\lambda_2$ " " " " CO.
$c_2/c_1$ = ratio of increase in concentration of $Se^0$ due to melting in CO.
$x$ = correction for scattering errors.

If no corrections were to be applied because of this scattering, the concentration ratio of increase of $Se^0$, according to Beer's law, would be as follows:

$$\text{Log } \frac{1}{T_2} = \frac{c_2}{c_1} \log \frac{1}{T_1}.$$

The added correction would be

$$(\text{Log } \frac{1}{T_2} + x) = \frac{c_2}{c_1}(\log \frac{1}{T_1} + x).$$

The ratio, $c_2$ to $c_1$, is constant, however, and other wave lengths may therefore be used as follows:

$$(\text{Log } \frac{1}{T_2} + x)(\log \frac{1}{T_1'} + x) = (\log \frac{1}{T_2'} + x)(\log \frac{1}{T_1} + x).$$

Using this equation for several wave lengths, $x$ is 0.032 for a specimen 1 cm. thick.

It is unfortunate that such correction had to be made because these assumptions reduce the curves, which are to be calculated subsequently for th ferrous, ferric, and polyselenide ions, to a semiquantitative basis. That is to say, the curves are calculated quantitatively but can be used only in a qualitative sense to show the trend of the reactions.

The transmittancy values at all wave lengths were divided by 100 to give $(I/I_0)$; the negative log of this value was then multiplied by the ratio of 10 to the thickness of the specimen in millimeters, and the correction of 0.032 was added at all wave lengths to selenium-containing glasses to give extinction curves for specimens 1 cm. thick. The curves so obtained are shown in Figs. 3 and 4 for the $K_2O{\cdot}Na_2O{\cdot}2CaO{\cdot}9SiO_2$ glasses melted in nitrogen and carbon monoxide, respectively. Curves for the same glass series melted in air and for the straight soda-lime series are almost identical to those in Fig. 3 except that the potash glass curves have smaller extinction values and those for the straight soda-lime glasses are slightly flatter.

Inasmuch as the curve for the red-colored selenium is known, the extinction values of the glass containing selenium and iron may be divided by the extinction values of the glass containing selenium alone at each wave length. At the wave length of minimum interference from ferrous, ferric, and polyselenide ions, therefore, a minimum value is obtained for this effect. This value closely approximates the increase in concentration of the red-colored elemental selenium. For the $2Na_2O{\cdot}2CaO{\cdot}9SiO_2$ glasses melted in air, this value was 2.23 and was found at a wave length of 650 m$\mu$. For the $K_2O{\cdot}Na_2O{\cdot}2CaO{\cdot}9SiO_2$ glasses melted in air, it was 3.67 and occurred at 560 m$\mu$; for those melted in nitrogen, it was 3.26 at 560 m$\mu$; and for those melted in carbon monoxide, the value was 0.888 (a decrease), which occurred at 770 m$\mu$. These values represent the maximum increase that $Se^0$ can undergo because, if they were larger, later calculations would show that the other absorbing ions in solution would have negative extinction values at some wave lengths.

Inasmuch as the concentration increase for the pink coloring component has been determined, the actual contribution of the $Se^0$ to the extinction curve for a glass may be calculated by multiplying the extinction values for the glass containing selenium alone at all wave lengths by the number of times the concentration has increased. When these increased extinction values are subtracted from those of the glasses containing both

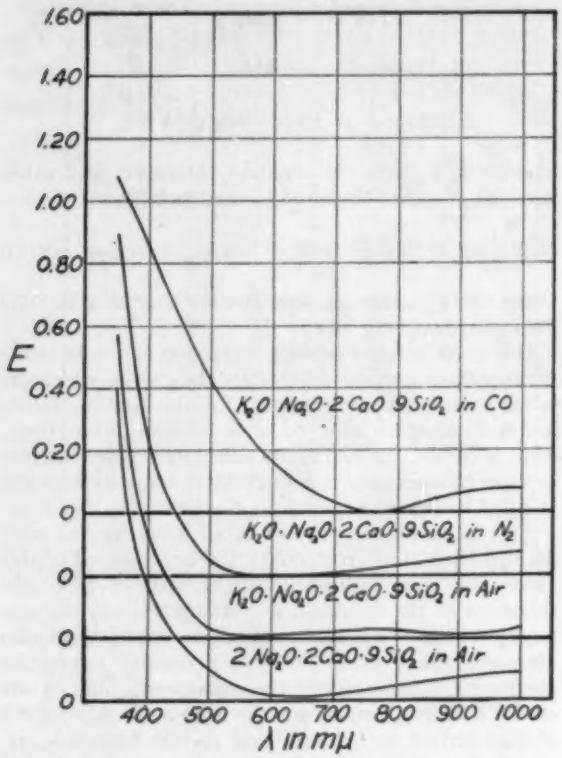


FIG. 7.—Extinction curves for constituents other than elemental selenium.

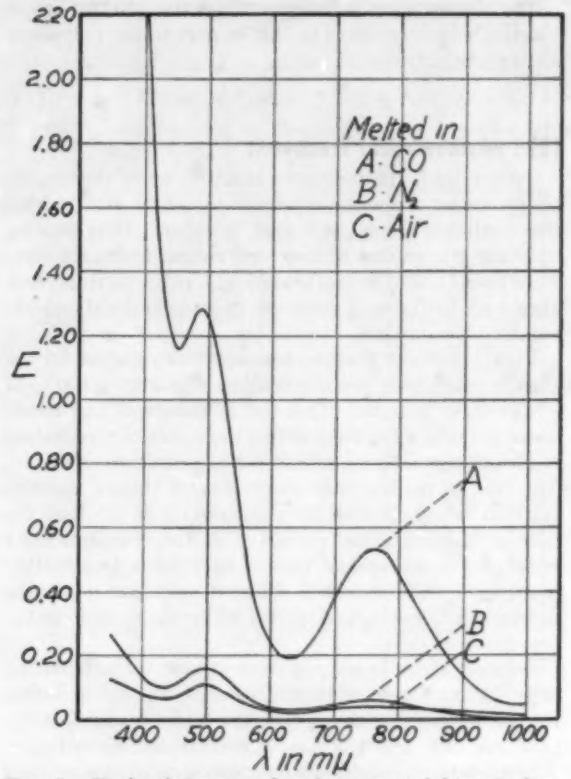


FIG. 8.—Extinction curves for glasses containing selenium alone.

iron and selenium, the resulting curve represents the other constituents in solution. Figure 7 shows these curves, which have been calculated for each series. A comparison of these curves, except that for the carbon monoxide melts, with those in Fig. 5 shows that there is a conversion of ferrous ions to ferric ions because the extinction values at the ferric end of the curve have increased whereas those at the ferrous end have decreased. Reaction (15) between iron and selenium is thus shown to be the most important of those yet obtained.

$$SeO_3^{=} + Fe^{++} \rightleftarrows Se^0 + Fe^{+++} \qquad (15)$$

A comparison of the curves in Fig. 7 with those of Fig. 6 indicates that the curve due to any polyselenide that may be formed is masked by the ferric ion curve and, under oxidizing conditions, a slight polyselenide formation may be present according to reaction (16).

$$Se^0 + Fe^{++} \rightleftarrows Se_x^{=} + Fe^{+++} \qquad (16)$$

To study the polyselenide ion, as assumed by Höfler,[4] all curves for the $K_2O\cdot Na_2O\cdot 2CaO\cdot 9SiO_2$ glass containing selenium and no iron were plotted together in Fig. 8. These curves show that less red coloring material is present in a glass melted in air than in one melted in nitrogen. Carbon monoxide, moreover, in its turn, produces much more elemental selenium than does nitrogen, but a sharp increase in the extinction values also occurs at the shorter wave lengths Treatment of the data with the same type of calculation as given for the iron-selenium equilibrium shows that melting in a carbon monoxide atmosphere, with the concentrations used in this case, is capable of increasing the pink coloring component 7.72 times and also of producing another coloring component. By multiplying the extinction values for the glass melted in nitrogen by 7.72 and by subtracting from the extinction values for the glass melted in carbon monoxide, the extinction curve is obtained for the component produced by melting in carbon monoxide. This curve is given in Fig. 9; a comparison with the curve for the polyselenide ion (in Fig. 6) shows that it may be due to the polyselenide ion. The small peak at approximately 760 mμ, which occurs at the same position as the usual $Se^0$ maxima, suggests that it is due to incomplete correction for the contribution of $Se^0$ to the curve; this error, in turn, is probably due to the assumption that equal scattering in all glasses containing selenium is not absolutely true.

Knowing these facts, the effect of iron on the selenium equilibria in glass melted in reducing atmospheres may be discussed. According to previous calculations, when a selenium glass is melted with iron in an atmosphere of carbon monoxide, the red coloring component decreases about 10%, whereas the brown components are greatly increased. This suggests the occurrence of primary reaction (17).

$$Se^0 + Fe^{++} \rightleftarrows Se_x^{=} + Fe^{+++} \qquad (17)$$

Another reaction, however, probably a slight one, such as reaction (18), may be present.

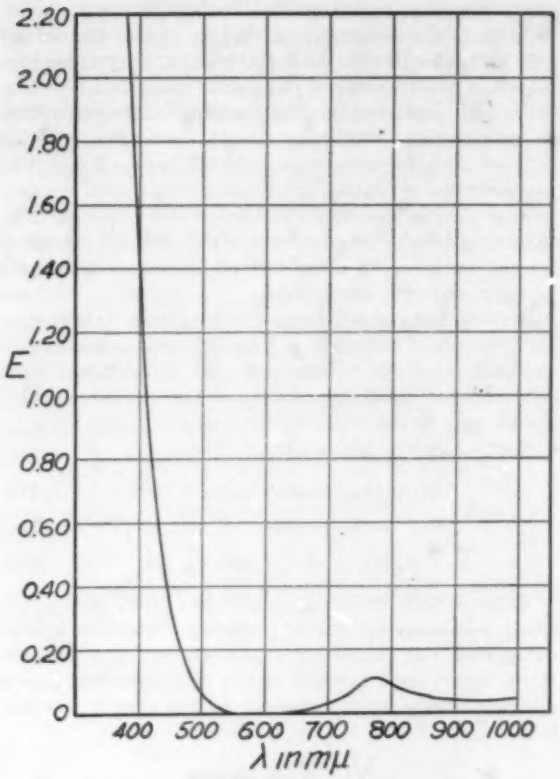


FIG. 9.—Extinction curve for polyselenide in glass.

$$SeO_3^{=} + Fe^{++} \rightleftarrows Se_x^{=} + Fe^{+++} \qquad (18)$$

## V. Discussion

In accordance with the work of Zachariasen,[8] Warren,[9] and others, glass is a liquid and should be treated as such. The current view of the structure of glass is one in which silicon, tetrahedrally surrounded by oxygen, forms a random lattice network. When the glass is fused quartz, all oxygens are connecting links between two silicons, and all silicons are connected to four other silicons by these oxygen links. When another oxide, such as $K_2O$, $Na_2O$, or CaO, is added to the fused quartz, each added oxygen breaks a silicon-oxygen-silicon bond and leaves two oxygens attached to silicon by one bond only. The cation which is introduced with the oxygen goes into the holes thus formed in the network and gathers about it (that is, coordinates) as many oxygens as it can. The resulting Ca–O and Na–O bonds are essentially ions, and the $Ca^{++}$ and $Na^{+}$ are cations.

The reactions will be written here in the form of ion equations because they are certainly ionic in character. The usual ions of aqueous solutions will be used in order to do this. It will also be necessary to use the symbol $O^{=}$, which is not an ion in the same sense that $Cl^{-}$ is an ion in aqueous solution, but an oxygen strongly bonded in the network of the glass. For those who prefer to use equations in the usual oxide form, however, the corresponding equation will be given.

When ferrous or ferric oxide is introduced into glass, the ions are obtained and are subject to oxidation and reduction just as they are in aqueous solution. Air will oxidize ferrous ions to ferric ions but will always leave some of them in the ferrous state; if all of the iron, moreover, is added to the batch as ferric oxide, the high temperature of the melting process will cause a partial reduction of ferric ions to the ferrous form, and oxygen is evolved to maintain electroneutrality as follows:

$$4Fe^{+++} + 4e \rightleftarrows 4Fe^{++} \qquad (19a)$$

$$\underline{2O^{=} - 4e \rightleftarrows O_2} \qquad (19b)$$

$$4Fe^{+++} + 2O^{=} \rightleftarrows 4Fe^{++} + O_2 \qquad (19c)$$

$$\text{or } 2Fe_2O_3 \rightleftarrows 4FeO + O_2 \qquad (19d)$$

When the conditions are more reducing, such as melting in a carbon monoxide atmosphere, more ferrous ions are produced.

$$2Fe^{+++} + 2e \rightleftarrows 2Fe^{++} \qquad (20a)$$

$$\underline{CO + O^{=} - 2e \rightleftarrows CO_2} \qquad (20b)$$

$$2Fe^{+++} + CO + O^{=} \rightleftarrows 2Fe^{++} + CO_2 \qquad (20c)$$

$$\text{or } Fe_2O_3 + CO \rightleftarrows 2FeO + CO_2 \qquad (20d)$$

When selenium is added to a glass batch and the glass is melted under neutral or slightly oxidizing conditions, the half-cell reaction (21) predominates.

$$SeO_3^{=} + 4e \rightleftarrows Se^0 + 3O^{=} \qquad (21)$$

When conditions are made more oxidizing, more colorless selenite is formed as follows:

$$Se^0 + 3O^{=} - 4e \rightleftarrows SeO_3^{=} \qquad (22a)$$

$$\underline{O_2 + 4e \rightleftarrows 2O^{=}} \qquad (22b)$$

$$Se^0 + O_2 + O^{=} \rightleftarrows SeO_3^{=} \qquad (22c)$$

$$\text{or } Se^0 + O_2 \rightleftarrows SeO_2. \qquad (22d)$$

When conditions are more reducing, more pink-colored elemental selenium is formed.

$$SeO_3^{=} + 4e \rightleftarrows Se^0 + 3O^{=} \qquad (23a)$$

$$\underline{2CO + 2O^{=} - 4e \rightleftarrows 2CO_2} \qquad (23b)$$

$$SeO_3^{=} + 2CO \rightleftarrows Se^0 + 2CO_2 + O^{=} \qquad (23c)$$

$$\text{or } SeO_2 + 2CO \rightleftarrows Se^0 + 2CO_2 \qquad (23d)$$

When conditions are still more reducing, brown-colored polyselenide is formed.

$$xSe^0 + 2e \rightleftarrows Se_x^{=} \qquad (24a)$$

$$\underline{CO + O^{=} - 2e \rightleftarrows CO_2} \qquad (24b)$$

$$xSe^0 + CO + O^{=} \rightleftarrows Se_x^{=} + CO_2 \qquad (24c)$$

$$\text{or } xSe^0 + CO + Na_2O \rightleftarrows Na_2Se_x + CO_2 \qquad (24d)$$

When iron and selenium are present together under neutral or slightly oxidizing conditions, the ferro-ferri and selenium-selenite half-cell reactions interact to produce more pink elemental selenium, fewer blue

[8] W. H. Zachariasen, "Atomic Arrangement in Glass," *Jour. Amer. Chem. Soc.*, **54** [10] 3841–51 (1932); *Ceram. Abs.*, **12** [4] 145 (1933).

[9] B. E. Warren, "X-Ray Diffraction Study of Structure of Glass," *Chem. Revs.*, **26**, 237–55 (1940); *Ceram. Abs.*, **19** [8] 187 (1940).

ferrous ions, and more of the less-colored ferric ions as follows:

$$4Fe^{++} - 4e \rightleftarrows 4Fe^{+++} \quad (25a)$$

$$SeO_3^{=} + 4e \rightleftarrows Se^0 + 3O^{=} \quad (25b)$$

$$4Fe^{++} + SeO_3^{=} \rightleftarrows 4Fe^{+++} + Se^0 + 3O^{=} \quad (25c)$$

$$\text{or } 4FeO + SeO_2 \rightleftarrows 2Fe_2O_3 + Se^0 \quad (25d)$$

Inasmuch as glasses which are decolorized by selenium are melted under these conditions, reaction (25) is particularly interesting because it shows the mechanism of selenium decolorizing. The concentrations of iron and selenium used in these melts are greater than those encountered in ordinary glasses; the same reaction is therefore assumed to occur when the concentration of both iron and selenium decreases. This reaction, moreover, has been established for only the particular base glasses used here, and again this reaction must be assumed to be similar in other base glasses.

When ferrous iron in a glass is oxidized to the ferric form, the glass is known to have less color; Kühl, Rudow, and Weyl[3] and Weyl[10] have emphasized this fact. The selenite ion, formed under oxidizing conditions, then oxidizes the ferrous ion to the less-colored ferric ion and at the same time produces some pink-colored selenium. All of the ferrous iron, however, is not oxidized to the ferric form, which is shown in Fig. 7 by the increasing extinction values at the longer wave lengths. This ferrous iron may possibly be compensated by the pink complimentary color of the elemental selenium.

The fact that a glass may be decolorized by an oxidation of ferrous ions is not a new concept. The decolorizing action of manganese, cerium, arsenic, and antimony has been attributed to their oxidizing action on ferrous ions.[3] In these cases, reactions occur as shown in (26) through (29).

$$Mn^{+++} + Fe^{++} \rightleftarrows Mn^{++} + Fe^{+++} \quad (26a)$$

$$\text{or } Mn_2O_3 + 2FeO \rightleftarrows 2MnO + Fe_2O_3 \quad (26b)$$

$$Ce^{++++} + Fe^{++} \rightleftarrows Ce^{+++} + Fe^{+++} \quad (27a)$$

$$\text{or } 2CeO_2 + 2FeO \rightleftarrows Ce_2O_3 + Fe_2O_3 \quad (27b)$$

$$AsO_4^{\equiv} + 2Fe^{++} \rightleftarrows AsO_2^{-} + 2Fe^{+++} + 2O^{=} \quad (28a)$$

$$\text{or } As_2O_5 + 4FeO \rightleftarrows As_2O_3 + 2Fe_2O_3 \quad (28b)$$

$$SbO_4^{\equiv} + 2Fe^{++} \rightleftarrows SbO_2^{-} + 2Fe^{+++} + 2O^{=} \quad (29a)$$

$$\text{or } Sb_2O_5 + 4FeO \rightleftarrows Sb_2O_3 + 2Fe_2O_3 \quad (29b)$$

As evidence cited by Höfler and Dietzel[4] in favor of the formation of ferrous selenide, the pink color increases during annealing, and the more reducing the conditions under which the glass is melted the more pink it becomes. Reducing conditions naturally favor the formation of the selenide and ferrous ions which then might produce more ferrous selenide, by mass action, during annealing.

$$Fe^{++} + Se^{=} \rightleftarrows FeSe \quad (30)$$

This phenomenon may be also explained by the oxidation-reduction mechanism in reaction (30). High temperatures and reducing conditions are known to favor the formation of the ferrous ion, and when the temperature is lowered, the ferrous ion tends to lose an electron and to revert to the low-temperature, chemically more stable ferric ion. When glasses containing iron and selenium are cooled, therefore, the ferrous ions may lose their electrons to selenite ions, thus reducing them and producing more of the pink-colored selenium. More reducing conditions should favor this reaction because they produce more reduced ferrous ions. The phenomenon of striking in the annealing ovens, in other words, may be due to a continuation of the oxidation-reduction decolorizing reaction which should be favored by the presence of more ferrous ions and, therefore, by more reducing conditions.

Several facts throughout the literature reveal that the presence of sulfate or of arsenic causes a decrease in the pink color due to selenium and also requires more selenium for good decolorizing. The action of these agents may be explained by reactions (31) and (32).

$$2AsO_4^{\equiv} + Se^0 \rightleftarrows 2AsO_2^{-} + SeO_3^{=} + O^{=} \quad (31a)$$

$$\text{or } As_2O_5 + Se^0 \rightleftarrows As_2O_3 + SeO_2 \quad (31b)$$

$$2SO_4^{=} + Se^0 \rightleftarrows SeO_3^{=} + 2SO_2 + O^{=} \quad (32a)$$

$$\text{or } 2SO_3 + Se^0 \rightleftarrows SeO_2 + SO_3 \quad (32b)$$

Some writers have suggested that the reaction between selenium and arsenic produces a selenium-arsenic compound, but this suggestion is to be taken with extreme reservation because it not only assumes that a selenium-arsenic compound forms but that it is colorless.

## VI. Conclusions

(1) When iron is introduced into a melted glass batch, equilibrium (19) is established:

$$Fe^{+++} + e \rightleftarrows Fe^{++} \quad (19)$$

If the atmosphere is reducing, the reaction is shifted to the right, and a blue-green glass is obtained, and if it is oxidizing, the equilibrium is shifted to the left, and a yellow-green glass results.

(2) If selenium is added to a glass that is melted under neutral or slightly oxidizing conditions, a pink color is obtained which is probably due to elemental selenium. As the melting conditions become more oxidizing, the pink color decreases according to a shift to the left in reaction (21).

$$SeO_3^{=} + 4e \rightleftarrows Se^0 + 3O^{=} \quad (21)$$

(3) With reducing conditions, the reaction is shifted to the right to produce more pink-colored selenium. When a carbon monoxide melting atmosphere is used, as opposed to a nitrogen atmosphere, a seven-fold increase in elemental selenium occurs. Reducing conditions also favor the formation of a brown-colored ion, which is probably polyselenide, according to a shift to the right in reaction (24*a*).

$$xSe^0 + 2e \rightleftarrows Se_x^{=} \quad (24a)$$

(4) When iron and selenium are present in a glass melted under neutral or slightly oxidizing conditions, the iron and selenite-selenium half-cell reactions interact as oxidizing and reducing agents to produce more pink color, less blue color, and more brown color (see reaction (25).

[10] W. Weyl, "Chemistry of Colored Glass, I–III," *Glass Ind.*, **18** [3] 73–78; [4] 117–20; [5] 167–71 (1937); *Ceram. Abs.*, **16** [6] 170; [7] 201; [8] 239 (1937).

$$4Fe^{++} - 4e \rightleftarrows 4Fe^{+++} \quad (25a)$$

$$SeO_3^{=} + 4e \rightleftarrows Se^0 + 3O^{=} \quad (25b)$$

$$SeO_3^{=} + 4Fe^{++} \rightleftarrows Se^0 + 4Fe^{+++} + 3O^{=} \quad (25c)$$

Molecularly, this reaction as indicated in the abstract is

$$Na_2SeO_3 + 4FeO \rightleftarrows 2Fe_2O_3 + Na_2O + Se^0$$

Part of the increase in brown color, under these conditions, may be due to the interaction between iron and selenium-polyselenide half cells.

$$2Fe^{++} - 2e \rightleftarrows 2Fe^{+++} \quad (33a)$$

$$xSe^0 + 2e \rightleftarrows Se_x^{=} \quad (33b)$$

$$xSe^0 + 2Fe^{++} \rightleftarrows Se_x^{=} + 2Fe^{+++} \quad (33c)$$

Molecularly, this reaction also may be written as indicated in the abstract,

$$xSe^0 + 2FeO + Na_2O \rightleftarrows Na_2Se_x + Fe_2O_3$$

As conditions become more reducing, the reaction producing polyselenide increases, and it predominates in an atmosphere of carbon monoxide. In neutral and slightly oxidizing atmospheres, the presence of iron leads to a two- to three-fold increase in the concentration of elemental selenium whereas melting in a carbon monoxide atmosphere causes a 10% conversion of elemental selenium to polyselenide by iron.

(5) The equation for the reaction between iron and selenite offers an explanation for the decolorizing action of selenium. Selenite ions oxidize ferrous iron to the less-colored ferric form, and this reduction of selenite produces more red-colored elemental selenium which may physically compensate as a complimentary color, for any ferrous ions remaining in solution.

(6) Soda-lime glasses show the same type of reactions as potash-soda-lime glasses except that their absorption curves are flatter and produce a glass that is slightly more yellow colored.

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# METALLURGICAL STUDY OF CAST IRON FOR GLASS MOLDS*

By W. H. Bruckner and H. Czyzewski†

Abstract

Research data are reported on the susceptibility of cast iron to cracking when it is used in molds for processing glassware. An accelerated test was run to produce cracking in a shorter time than would occur in the production of glassware. The results from this test indicate that sand-cast iron is more resistant to cracking than chill-cast iron of the same composition. The alloyed chill-cast irons, however, cracked less severely than the unalloyed iron. An annealing heat-treatment of these irons increased resistance to cracking, whereas a spheroidizing heat-treatment reduced resistance. A maximum resistance to cracking together with the ability of the iron to take a high polish apparently may be obtained by using an annealed, chill-cast alloy iron containing chromium, nickel, and molybdenum. Such iron is more susceptible to cracking than a sand-cast iron of the same composition, but the latter type is incapable of a sufficiently high polish and usually has an open, porous structure.

## I. Introduction

The study of cast iron for glassforming molds, at a suggestion from Parmelee,* was undertaken in 1938 by the Department of Mining and Metallurgical Engineering. The object of the study was to improve the service life of cast-iron molds which are employed in automatic glassforming machines.

The most frequent cause of mold failure is the development of cracks in that part of the working surface which is alternately in contact with the hot glass and then cooled by various methods. Glass molds have a considerable mass to provide a heat reservoir and to produce a uniform temperature around the ware during the operation of the glassforming machines.

The body of the mold remains at substantially the same temperature, owing to its large mass, whereas the working surface is subjected to heating cycles but is restrained from undergoing normal thermal expansion on heating and contraction on cooling. The mold surface, therefore, goes through alternate cycles of tension and compression; the cracking at the working surface may thus be classified as a fatigue failure.

A fatigue test is usually made over a range of applied stress to obtain a so-called S–N diagram or curve for the material being studied. Such a curve is shown in Fig. 1, and it indicates that the specimen will withstand a greater number of reversals of stress before failure occurs because the intensity of the alternately applied stress is reduced. A reduction in the mass of the glass mold would reduce the intensity of the stress, which would restrain the working surface from under-

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* C. W. Parmelee, Head of the Department of Ceramic Engineering, University of Illinois, Urbana, Ill.

This research study has been continued since 1938 and has been carried out by senior students in Metallurgical Engineering, who have undertaken the work as their thesis problem.

going its normal expansion and contraction, and therefore should increase the service life of the mold if all of the conditions remain the same as those for the more massive mold.

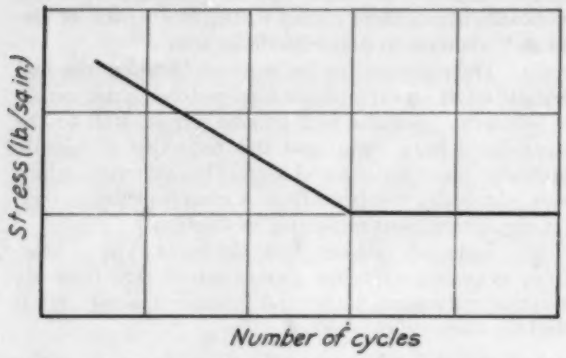



FIG. 1—S-N curve obtained in determining endurance limit.

An accelerated test has been established[1] to determine the susceptibility of various types of cast iron to cracking when they are heated and cooled. The test consists of heating cylinders of cast iron, 2 in. long and 2 in. in diameter, to 1100°F. and quenching in water at room temperature. The test specimens are cycled in this manner until failure occurs; such failure requires a much smaller number of cycles than when cast iron is used in the glass mold. The decrease in temperature of the blank mold surface during the cooling cycles is estimated as approximately 200° to 300°F. from a maximum temperature of 1100° to 1250°F. during the glassforming cycle. This decrease is small when compared with the cycle of 1100° to 80°F. in the accelerated cracking test.

Data are reported here for a series of plain and alloy cast irons in the chill-cast and sand-cast condition which were subjected to the accelerated cracking test. Studies were also made on the effect of modifying the microstructure of the cast irons by heat-treatment.

## II. Materials

Blocks of cast iron, 6 by 9 by $2^1/_2$ in. in size, were used.* The analyses of the irons are given in Table I in which the T series was plain iron, cast with one 6- by 9-in. face against a chiller, which was made from a cast-iron block of the same dimensions as the casting. The S series was sand-cast alloy iron. The C series, which duplicated the S series in chemical content, was cast with one 6- by 9-in. face against a chiller as was also the T series. The T series, with decreasing silicon content, was intended to give increasing amounts of pearlite or combined carbon.

A number of blank suction molds,† which had failed at a small number of cycles, was examined to determine the cause of their early failure.

## III. Procedure

Cylinders of cast iron, 2 in. long by 2 in. in diameter, were machined from the blocks. One flat face of the cylinders from the chill irons contained the chill surface of the original casting with just sufficient metal removed to produce a smooth finish. The cylinders were drilled, and a tapped hole was provided in the face opposite the chilled face to take a threaded rod, $^1/_4$ in. in diameter, from which the specimens were suspended during the cracking test. Specimens of the same size were cut from the sand-cast blocks, and one flat face of the cylinder contained the original sand-cast surface machined to a smooth surface. The opposite flat face contained the drilled and tapped hole for the suspending rod (shown in Fig. 2, which illustrates the fixture used to suspend the test specimens).

The specimens were then heated to 1100°F. and cooled in water until severe cracking occurred. Observations were made of the number of test cycles required before the specimens started to crack. The "as-cast" irons, TF1, TP1, and TP2 were subjected to this test (see Table II), but no observations were made of the number of cycles required to start cracking.

The specimens were tested with the following series of heat-treatments carried out before they were subjected to the accelerated cracking test: (1) The "as-cast" condition without heat-treatment; (2) the annealed condition, wherein the chill-cast irons of series T and C were heated slowly to 1450°F., held at this temperature for 4 hours, and furnace cooled; (3) the spheroidized condition, in which all of the chill- and sand-cast iron specimens were heated slowly to 1280°F.,

TABLE I
CHEMICAL ANALYSIS OF CAST-IRON SAMPLES

| | C | Si | Mn | Ni | Cr | Mo |
|---|---|---|---|---|---|---|
| TF1 | 3.61 | 2.99 | 0.67 | | | |
| TP1 | 3.55 | 2.76 | .66 | | | |
| TP2 | 3.60 | 2.50 | .66 | | | |
| SA1 | 3.39 | 2.23 | .68 | 1.25 | 0.45 | 0.50 |
| SA2 | 3.57 | 1.50 | .68 | 1.20–1.50 | | 0.20–0.30 |
| SA3 | 3.50 | 2.02 | .65 | | | 0.35–0.45 |
| CA1 | 3.44 | 2.40 | .66 | 1.25 | 0.45 | 0.50 |
| CA2 | 3.57 | 1.50 | .68 | 1.20–1.50 | | 0.20–0.30 |
| CA3 | 3.50 | 2.00 | .80 | | | 0.35–0.45 |

TABLE II
NUMBER OF CYCLES AT 1100° TO 80°F. BEFORE CRACKING OCCURS

| | As cast (1) | Annealed (2) | Spheroidized (3) | Maximum pearlite (4) |
|---|---|---|---|---|
| TF1 | | 1–2 | 1–2 | 3 |
| TP1 | | 7–8 | 1–2 | 2 |
| TP2 | | 3–4 | 4 | 4 |
| SA1, SA2, and SA3 | Slight cracking at 40 | | Fine cracks at 7–8 | |
| CA1 | 8–9 | 22–23 | 5 | 8–9 |
| CA2 | 5–6 | 5–6 | 1–2 | 5 |
| CA3 | 4 | 6 | 1–2 | 2 |

[1] W. H. Bruckner, L. R. Kovac, and A. B. Wilder, "Metallurgical Study of Cast-Iron Glass Molds," *Bull. Amer. Ceram. Soc.*, 19 [2] 58–61 (1940).

* Supplied by D. P. Forbes, president of the Gunite Foundries Corporation.

† Supplied by Ball Brothers Company through F. G. Passotti.

FIG. 2.—Equipment for accelerated cracking test on cast-iron specimens.

held at this temperature for 100 hours, and furnace cooled; and (4) the quenched and drawn condition in which the chill-cast irons of series T and C were heated slowly to 1650°F., quenched in oil, reheated to 1280°F., and furnace cooled.

At the conclusion of the cracking test, a study was made of the microstructure and the type of cracking which occurred. Hardness tests were made on the as-cast irons to determine the hardness gradient across the chill- and sand-cast region as compared with the hardness gradient occurring in actual blank molds.

## IV. Discussion of Data Obtained

Table II gives a summary of the results of the accelerated cracking tests in terms of the number of cycles (heating to 1100°F. and cooling to 80°F.) required to initiate cracking. Of the cast irons in the as-cast condition, the sand-cast series, SA1, SA2, and SA3, had the highest resistance to cracking. The cracks which formed during 40 test cycles were superficial, but they were numerous and presented a network appearance. Of the chill-cast irons in the as-cast condition, the alloy series C was approximately as resistant to cracking as were the plain irons of series T; the cracks in specimens of the T series, however, were more severe than those in the alloy irons, CA1 and CA2. The appearance of the flat surfaces at the ends of the cylinders for all of the chill-cast irons after 20 cycles of testing are shown in Fig. 3.

The annealing heat-treatment was the most effective for the CA1 iron in increasing the resistance to cracking.

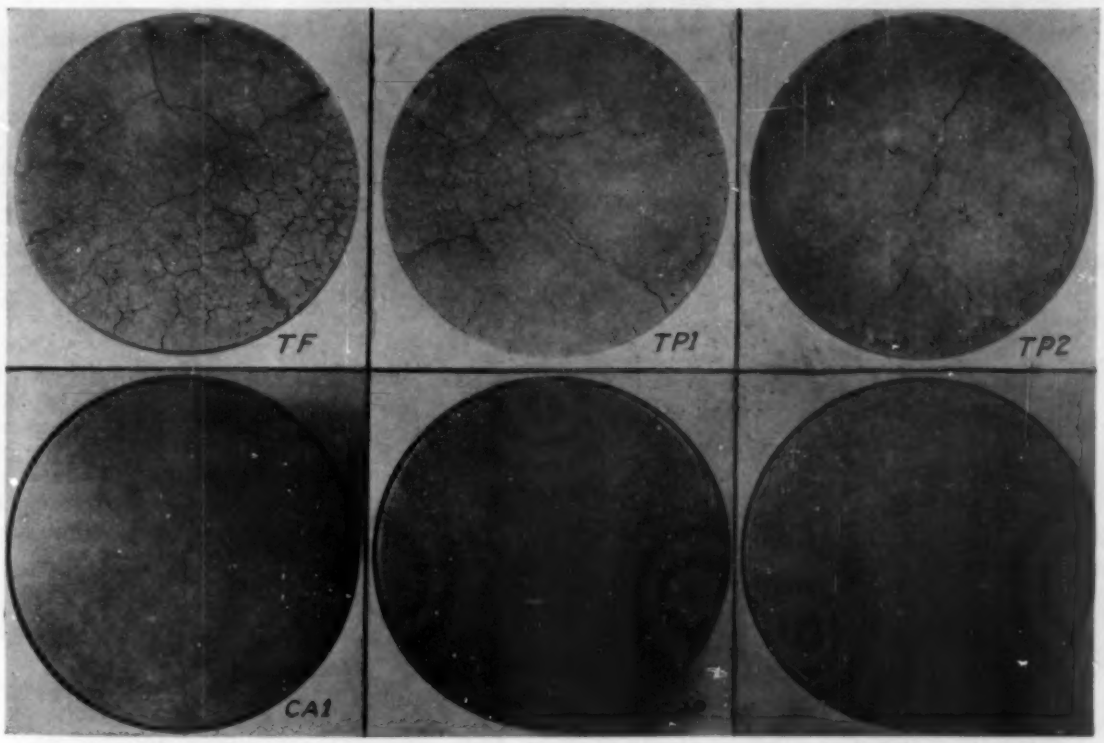



FIG. 3.—Appearance of chill-cast iron specimens subjected to accelerated cracking test for 20 cycles.

The CA1 alloy iron had the highest resistance to cracking of any of the chill-cast irons tested; in the annealed condition, the resistance of this iron to cracking approached that of the sand-cast alloys.

The spheroidizing heat-treatment, which was applied to all of the chill- and sand-cast irons, definitely reduced the resistance to cracking below that in the as-cast condition. The specimens, which were heat treated for maximum pearlite in the quenched and drawn condition, had approximately the same resistance to cracking as the as-cast irons. The results given in Table II, therefore, show the basic resistance of the cast irons in the as-cast condition as well as the effect of three heat-treatments which improve, reduce, or do not affect the resistance to cracking.

## V. Microstructure

The most obvious difference in microstructure in the as-cast condition is shown by a comparison of the chill-cast and the sand-cast irons. Figures 4 and 5 illustrate this difference for the CA1 (chill-cast) and SA1 (sand-cast) alloy iron. These figures also show the distribution and size of the graphite flakes in the unetched condition, and the amount and distribution of combined carbon as pearlite and the peppered areas of higher phosphorous content are revealed by etching the polished surface.

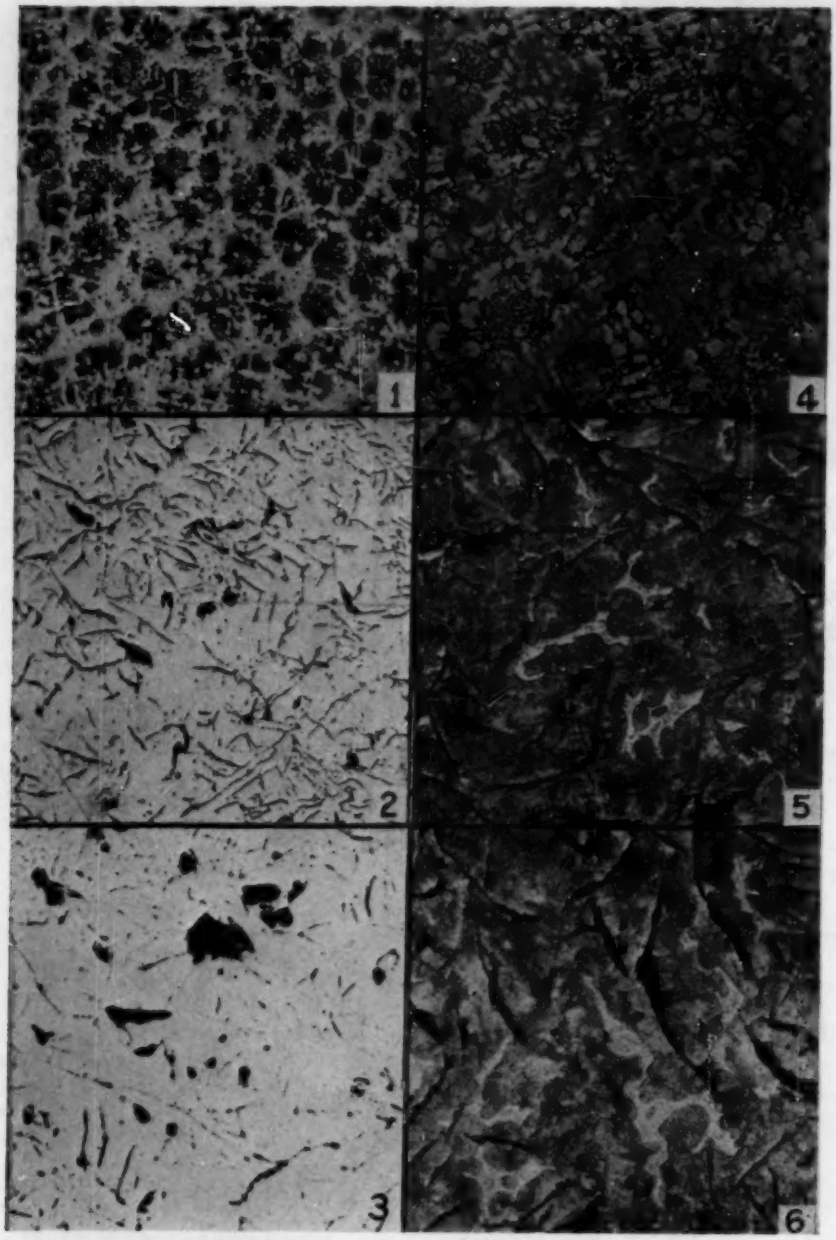
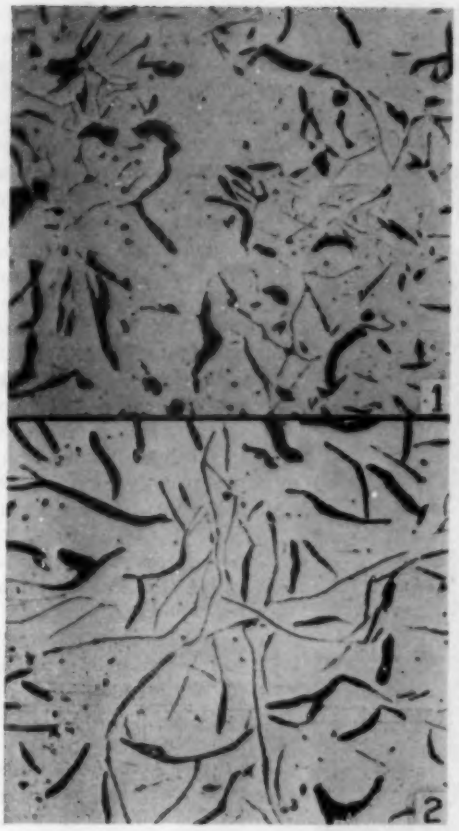
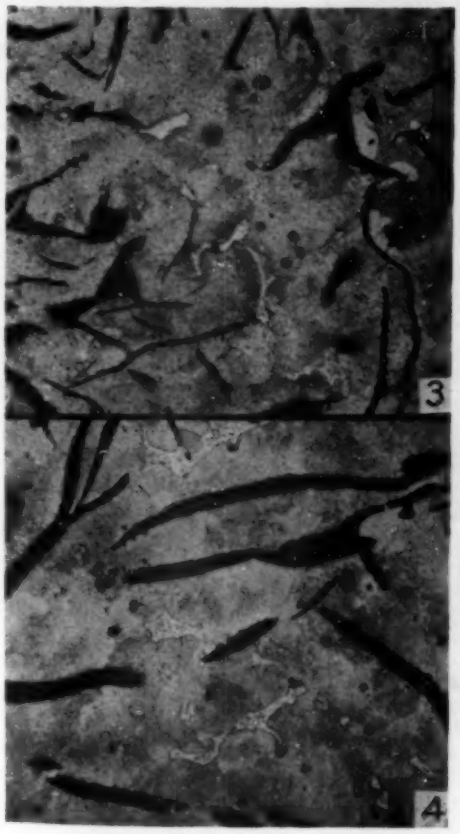



FIG. 4.—Microstructures of chill-cast alloy iron, CA1; "as polished" structures (1), (2), and (3) show graphite size and distribution, ×50; etched structures (4), (5), and (6) show distribution and amount of graphite, pearlite, ferrite, and high phosphorous area, ×150; (1) and (4), CA1A; (2) and (5), CA1B; (3) and (6), CA1C.

For the chill-cast iron, CA1, the three regions illustrated are (1) A, the chill region, (2) B, the center, and (3) C, the sand-cast region of the $2^1/_2$-in. thick block which was chill-cast on one face. The colonies of finely divided graphite in region A are characteristic of the microstructure of a chilled casting generally used for glassforming molds. Such a surface may be polished to a high degree. The increase in the size of the flakes of graphite and in the amount of pearlite is shown in regions B and C as the distance from the chilled face increases.

For the sand-cast iron, SA1, two regions are illustrated in Fig. 5, namely, (1) E, the sand-cast area and (2) C, the center of the block, which was $2^1/_2$ in. thick. The graphite flakes are somewhat smaller at the sand-cast edge, and a slight increase in pearlite is evident. Owing to the large size of the graphite




and the occasional porosity of the sand casting, a smooth, polished surface free from imperfections cannot be obtained. In spite of their high resistance to cracking, the sand-cast irons cannot be used for glass-forming molds because of their inability to take the high polish necessary at the working face in contact with hot glass.

A comparison of the microstructure of the three chill-cast alloy irons is given in Fig. 6 for the chill area A. There appears to be a trend toward an increasingly dendritic structure in the order CA1, CA2, CA3, which is also the order of highest to lowest resistance to cracking. In the sand-cast alloys (Fig. 5), there is practically no evidence of dendritic structure for the SA1 iron, which is undoubtedly one reason for the high resistance of the sand-cast irons to cracking.

The effect of the heat-treatments in modifying the microstructure is shown in Fig. 7 for the CA1 alloy only because of its high resistance to cracking. The study of the heat-treated structures was made after the specimens had been subjected to the accelerated cracking test which, however, had no perceptible effect on the microstructure. The chill area A of annealed iron CA1 is shown in (2) of Fig. 7, and the structure consists of graphite, ferrite, and pearlite partly in lamellar and partly in spheroidal form. The pearlite was probably spheroidized to the slight degree shown by the slow cooling from the annealing temperature. The chill area A of the spheroidized CA1 iron is shown in (3) of Fig. 7 and consists entirely of spheroidized pearlite, ferrite, and graphite. The large amount of free ferrite contained in the spheroidized irons is considered to be the chief cause of their low resistance to cracking, inasmuch as a ferrite matrix has a lower strength than one consisting of pearlite. The chill area A of the quenched and drawn CA1 iron is shown in (4) of Fig. 7 and consists almost entirely of fine pearlite and graphite. The structure resulting from this heat-treatment appeared to be ideal for resisting the stresses applied in the accelerated cracking test. The reason for its low resistance to cracking is not apparent because an improved resistance over that of the "as-cast" iron was expected on the basis of the relief of casting stresses alone.

The paths of the cracks occurring in the chill-cast iron were studied, and that shown in Fig. 8 for the CA1 iron is typical of the group. The crack progresses from the chill surface (right side of Fig. 8) to the interior from one graphite cluster to another and along the dendrites which have formed normal to the chill surface. At the end of 20 cycles of the accelerated test, some of the cracks have progressed to approximately $1^1/_4$ in. from the chill surface, which is the greatest depth of chill. Further progress of cracking tends toward branching of the cracks almost normal to the main crack in the more slowly cooled portion of the casting where a dendritic structure no longer appears. The dendrites in the chill-cast iron appear to constitute directions of weakness which promote the easy progress of a crack.

FIG. 5.—Microstructure of sand-cast alloy iron SA1; (1) SA1E and (2) SA1C, as polished, ×50; (3) SA1E and (4) SA1C, etched with 5% Nital, ×150.

## VI. Physical Properties

The hardness gradients over the cross section of the cast-iron blocks are given in Figs. 9 and 10 for the chill- and sand-cast blocks, respectively. The same gradients determined after heat-treatment of the CA1 iron are shown in Fig. 11. Figure 9 shows that the CA1 iron has the highest hardness of the alloy, chill-cast irons; this composition in the SA1 iron also produces the maximum hardness of the series. The A3 alloy in the chill or sand-cast blocks has the minimum hardness of the series. The effect of heat-treatment on the hardness gradient is shown in Fig. 11, where curve CA1 indicates that the iron in the as-cast condition has the maximum hardness. The quench and draw heat-treatment, represented by specimen PNCA1, produced the least change in hardness whereas the spheroidizing treatment, represented by NCA1S, softened the iron to the greatest extent; the annealing heat-treatment, represented by ACA1, had an intermediate effect in reducing hardness. The lower portion of this curve shows the general spread in hardness values which was usually found in the more slowly cooled portion of the castings, remote from the chill, because of the general porosity encountered.

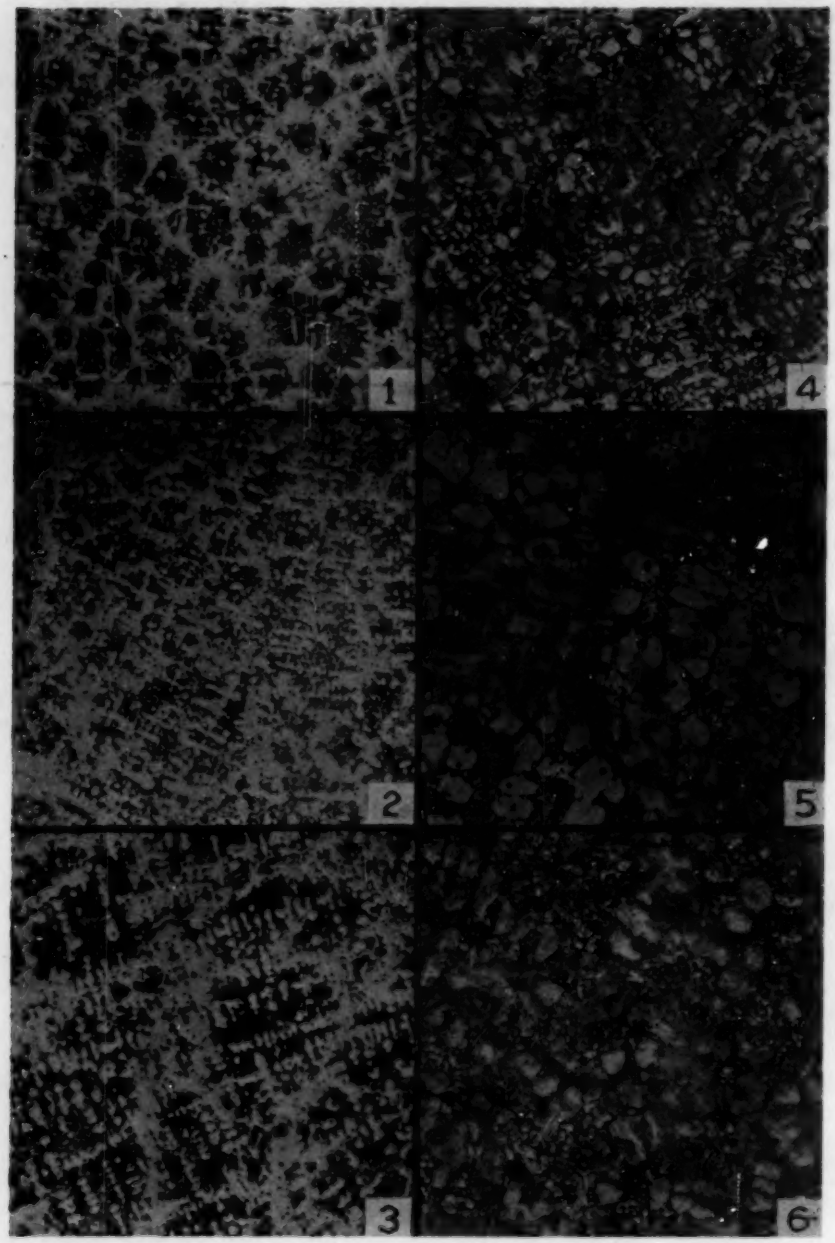



FIG. 6.—Microstructures of chill-cast alloy irons CA1, CA2, and CA3 in the chill area A; (1), (2), and (3) are CA1A, CA2A, and CA3A, respectively, as polished, ×50; (4), (5), and (6) are CA1A, CA2A, and CA3A, respectively, etched with 5% Nital, ×150.

Hardness gradients, which were determined on several glass molds of chill-cast, unalloyed irons, cross sectioned for the purpose of examination, show that the maximum hardness is less than that attained in the blocks of chill-cast iron. This effect is attributed to the large amount of free ferrite normally present at the working surface of the chilled-iron glass mold. The decrease in hardness with distance is more rapid in the actual mold than in the blocks of chill-cast iron owing to the greater porosity of the mold iron and to the more rapid increase in the flake size of the graphite with decreasing cooling rate

## VII. Examination of Glassforming Molds

The micrographic examination of blank suction molds, which failed by cracking after a short time in operation, indicated that the pearlite throughout the chill and slowly cooled portions was almost completely spheroidized. The time that

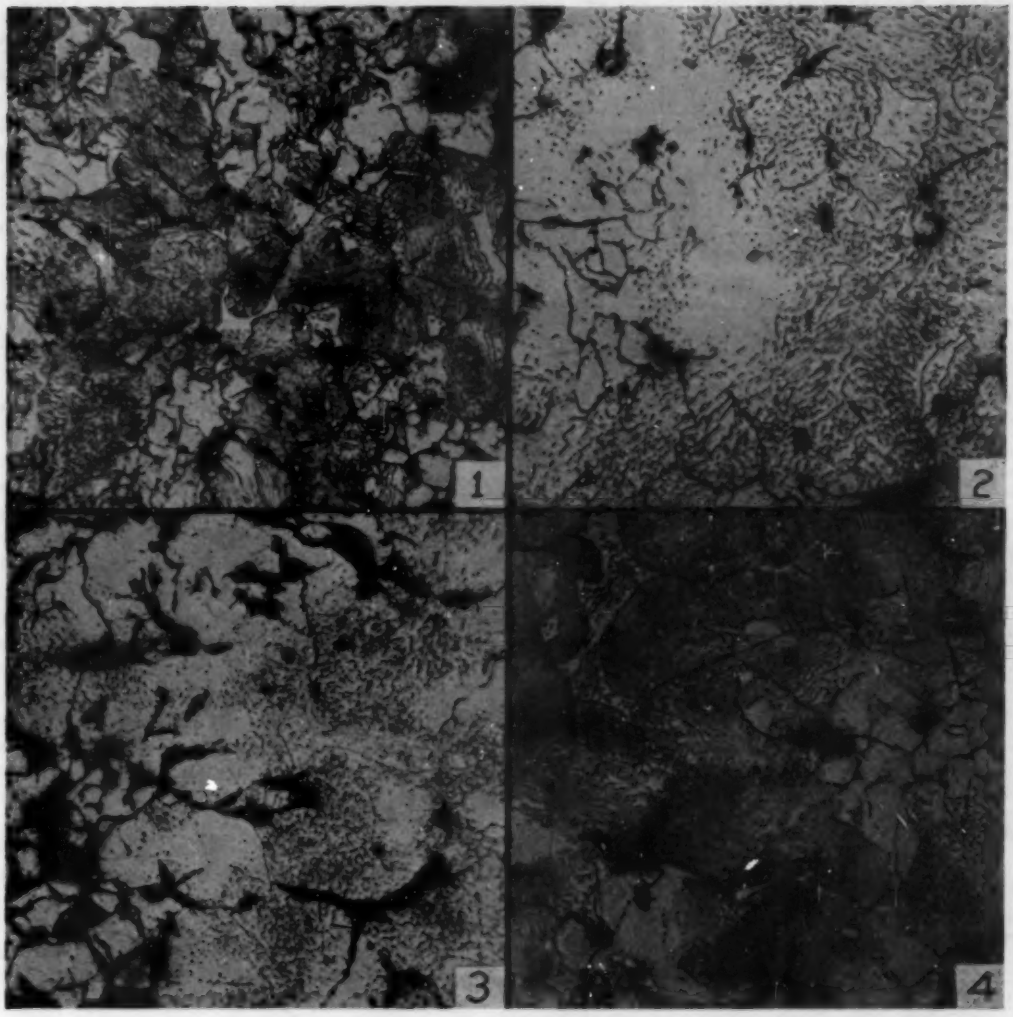



FIG. 7.—Microstructures of heat-treated CA1 iron etched with 5% Nital, ×500; (1) as-cast; (2) annealed; (3) spheroidized; (4) quenched and drawn.

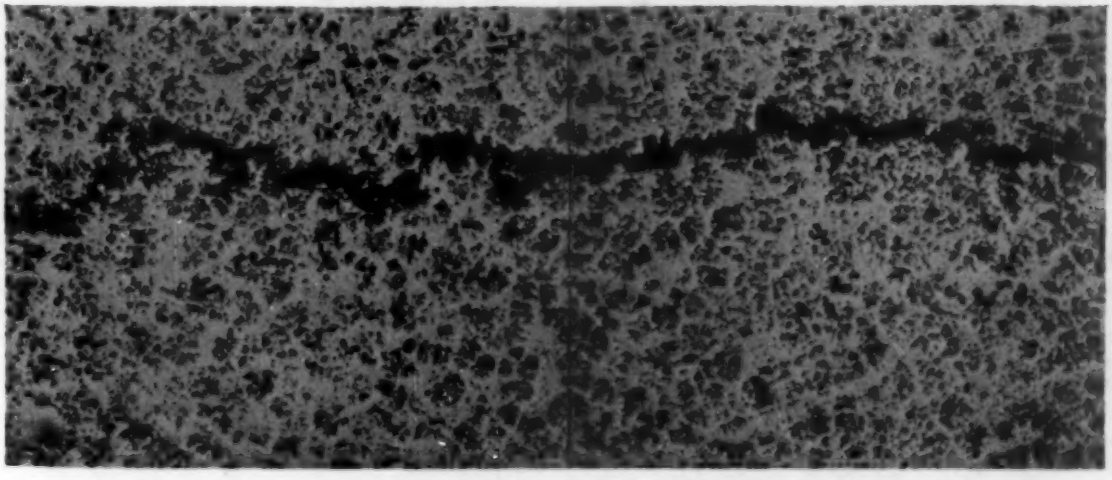


FIG. 8.—Progress of crack through chill area of specimen CA1.

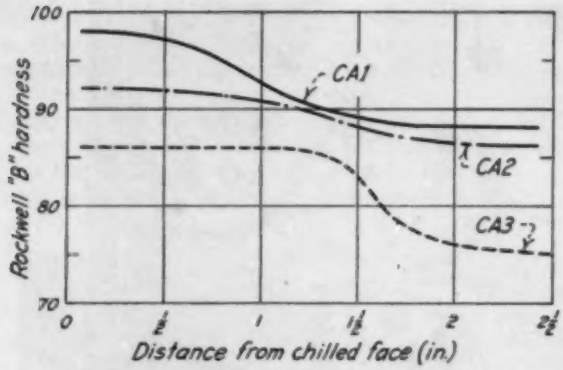



FIG. 9.—Hardness gradients in chill-cast alloy irons.

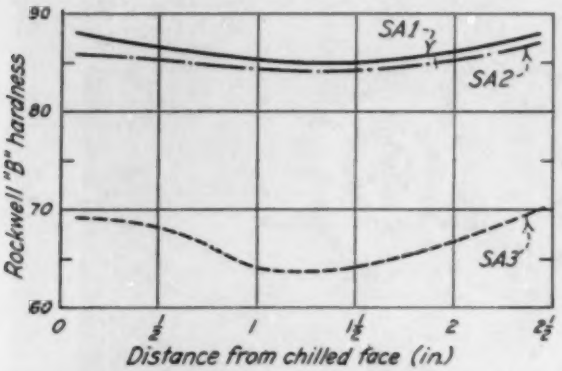



FIG. 10.—Hardness gradients in sand-cast alloy irons.

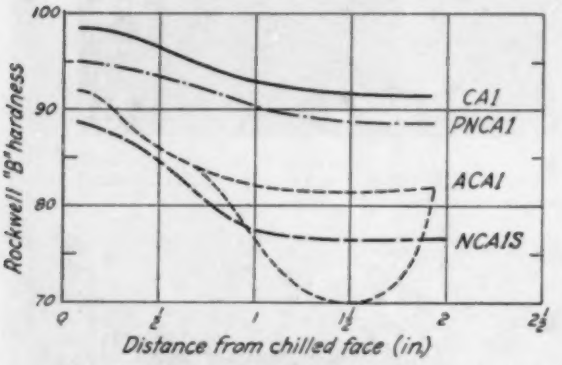



FIG. 11.—Hardness gradients in chill-cast alloy iron CA1 before and after heat-treatment.

the molds were in service was so short as to preclude any possibility of their having been spheroidized during their brief service life. The molds appeared, therefore, to have been given a spheroidizing heat-treatment to improve their machinability. The results of the accelerated cracking test show that cast iron in the spheroidized condition had the lowest resistance to cracking; the spheroidizing heat-treatment, which the molds received, therefore, did not develop their maximum resistance to cracking.

## VIII. Summary and Conclusion

Sand-cast iron of the composition studied is most resistant to cracking during the alternate heating and cooling of the accelerated cracking test. The advantages of such an iron, which contribute to the high resistance, are the lack of a definitely dendritic structure and the uniformity of the microstructure and physical properties over the cross section of the casting. The microstructure of the sand-cast irons (as cast) consists mainly of coarse graphite, lamellar pearlite, and varying amounts of ferrite. The lamellar pearlite contributes to the high resistance to cracking because a spheroidizing heat-treatment, which transforms the lamellae to spheroidal form, reduces the resistance to cracking. The sand-cast irons, however, have an open, porous structure, and it is not possible to polish the surface to the degree required for the working surface of a glassforming mold.

Chill-cast irons that are subjected to the accelerated cracking test show an early failure, and the cracks formed are relatively fewer and more severe than those formed in a sand-cast iron of the same composition. The severity of cracking in chill-cast alloy irons is less than that in the chill-cast plain irons, although the initial cracking in both irons takes place in approximately the same number of cycles. The use of the three metals, nickel, chromium, and molybdenum, as additions to the chill-cast iron produces a superior product which is most resistant to cracking. The response of this chill-cast, alloy iron to an annealing heat-treatment is such as to give a greatly improved resistance to cracking.

The formation of an entirely ferritic matrix in the cast irons by means of a spheroidizing heat-treatment reduces the resistance of the irons to cracking. The formation of a matrix of fine lamellar pearlite by means of a quench and draw heat-treatment gives the chill-cast irons no increased resistance to cracking over that of the as-cast iron. The spheroidized and the quenched and drawn iron had been relieved of stress at 1280°F., and they represent, therefore, the minimum and maximum strength of the matrix, respectively, under comparable conditions. The respective hardness values in Fig. 11 indicate this condition of strength.

The hardness of the annealed iron is intermediate between that of the iron in the spheroidized and the quenched and drawn condition. The microstructure of the annealed iron is also intermediate between that of the latter two irons. The matrix is composed of free ferrite, partially spheroidized pearlite, and lamellar pearlite, which apparently gives a desirable combination of ductility in the ferrite for absorption of the thermal shock and high strength in the lamellar pearlite to resist the spread of cracks. Accurate control of the annealing operation would therefore appear to be necessary to attain a balanced microstructure for maximum resistance of the glass mold to cracking in service.

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# TRANSVERSE TESTING FURNACE*

By J. C. McMullen

Abstract

An electric furnace is described, designed for determining the transverse strength of 9-in. brick to temperatures as high as 1500°C. It is especially useful when a large number of brick are to be tested because the samples, which have been preheated in a second furnace, may be easily introduced and withdrawn while the furnace is held at breaking temperature.

## I. Introduction

The furnace herein described was designed primarily as a convenient and accurate means of determining the hot modulus of rupture on refractory brick. An oil-fired furnace was previously used for this purpose, similar to that described for high-temperature load testing.[1]

## II. Description of Furnace

### (1) The Furnace

Figure 1 shows a cross section of the heating chamber. The 12- by 14- by 22-in. chamber is lined with $4^1/_2$ in. of high-grade fire-clay brick backed up by $2^1/_2$ in. of Sil-O-Cel brick, all laid in a silicate cement. The shell is formed of No. 10 gauge sheet iron, held in place by an angle-iron frame, $2^1/_2$ by $2^1/_2$ by $^1/_4$ in. in size. Beneath the furnace is located a pneumatic cylinder, a pressure gauge, and control valves. The lever arm is made of 3- by $^3/_4$-in. cold-rolled steel. The furnace is heated with twelve nonmetallic heating elements, spaced to give uniform temperature throughout the breaking chamber. The hinged door, being small, may be opened and closed quickly so that little heat is lost on transferring the test brick. Figure 2 shows a photograph of the furnace.

### (2) Breaking Mechanism

The refractory plunger, which has a cross section of $1^1/_4$ by $4^1/_2$ in., is actuated in a horizontal direction. The load to break the brick is supplied by a 4-in. diameter pneumatic cylinder through a lever arm to the plunger. With 100 lb. per sq. in. of air pressure available and a lever ratio of 5 to 1, a load of 6280 lb. may be applied to the brick. On a $2^1/_2$- by $4^1/_2$- by 9-in. brick, the maximum modulus of rupture value possible is more than 2600 lb. per sq. in.

$$MR = \frac{3PL}{2bd^2} = \frac{3 \times 6280 \times 8}{2 \times 4.5 \times (2.5)^2} = 2680 \text{ lb./in.}^2$$

## III. Method of Testing

The furnace chamber is large enough that three brick may be heated simultaneously within it, one in a breaking position and the other two in the adjacent space. If a larger number of specimens are to be tested, a preheating furnace is used, and the lot is heated to 100°C.

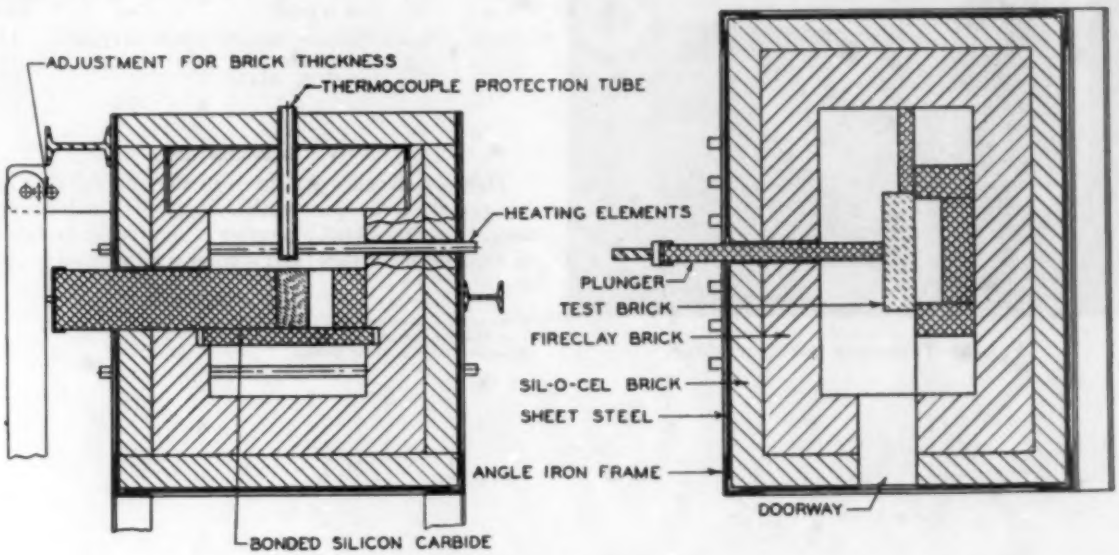


Fig. 1.—Cross section of heating chamber.

* Presented at the Forty-Fourth Annual Meeting, The American Ceramic Society, Cincinnati, Ohio, April 21, 1942 (Refractories Division). Received July 10, 1942.

[1] "A.S.T.M. Tentative Method of Testing Fire Clay and Alumina-Diaspore Refractories Under Load at High Temperatures," 1939 A.S.T.M. Book of Standards [Part II], pp. 959–62; diagram of furnace, p. 159.

or so below the breaking temperature. By preheating slightly lower rather than at the same temperature as the breaking temperature, all brick may be held the same length of time at the breaking temperature. If the preheating temperature is too much below that of the breaking temperature, spalling is apt to occur during the transfer. The brick are transferred one at a time through a small door in the front side of the transverse furnace to the breaking hearth. Each brick, laid on its $2^1/_2$- by 9-in. side, slides on the hearth until it rests in front of two refractory abutments whose inner faces are spaced 8 in. apart. The hearth is covered with a light coating of sand to prevent the test brick from sticking to the hearth. To break the brick, air is bled through a small orifice into the cylinder operating the plunger and escapes through an exit line controlled by a needle valve. The pressure in the cylinder is increased as the needle valve is closed. The rate of pressure applied should be kept constant from test to test.

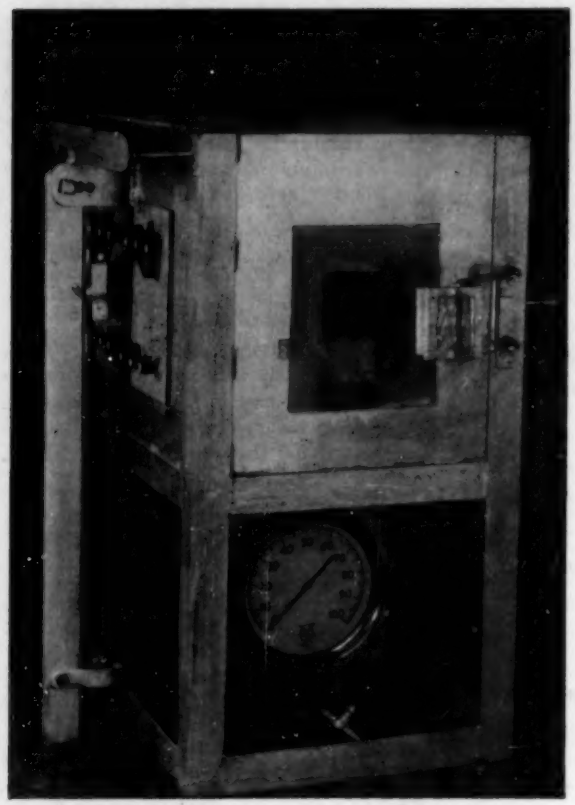

FIG. 2.—Transverse testing machine.

## IV. Temperature Conditions

### (1) Furnace Control

The furnace can be heated to 1350°C. in three hours, using 20 kw., and it requires 13 kw. to hold at that temperature. The temperature can be most accurately maintained by using a variable voltage transformer. A sufficiently accurate control may be maintained, however, by using a 110-volt source of power regulated by a make-break mechanism. The power input may also be regulated by a switch arrangement to give various combinations of series or series-parallel connections to the heating elements.

### (2) Temperature Equilibrium in Test Brick

Before breaking, the brick are allowed sufficient time to reach temperature equilibrium after they have been transferred from the preheating furnace. This interval depends on the type and thickness of the brick being tested. In cases in which one test brick is to be broken and heated in the test furnace, this temperature lag from the outside to the inside of the brick is not so great. Table I shows data obtained on the length of time required to reach equilibrium at 1350°C. on several kinds of brick. These test pieces were drilled so as to allow the hot junction of a thermocouple to be placed at the center. While the breaking furnace was held at 1350°C., the length of time for the center of the brick to reach equilibrium was noted. On breaking the brick, the plunger is partially withdrawn to permit the removal of the broken pieces. The ease of introduction and withdrawal while the brick are hot makes it possible to break a large number of samples in a comparatively short time.

TABLE I

TIME REQUIRED TO REACH EQUILIBRIUM

| Preheating treatment | Type of brick | Size | Minutes to reach equilibrium |
|---|---|---|---|
| 1250°C. | Bonded silicon carbide | 9-in. straight | 15 |
| " | " alumina | " " " | 18 |
| " | Fire clay (70% $Al_2O_3$) | " " " | 51 |
| " | " " " | " " split | 35 |

## V. Conclusions

This test furnace has been in use during 1941 and has proved to be quite satisfactory. It produces consistent results, allows a number of samples to be broken in a minimum of time, and is compact and easy to operate.

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